Fouling mitigation in coagulation microfiltration hybrid system for drinking water treatment

Sadreddini, Sara

2009

Sadreddini, S. (2009). Fouling mitigation in coagulation microfiltration hybrid system for drinking water treatment. Master's thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/19917>

<https://doi.org/10.32657/10356/19917>

FOULING MITIGATION IN COAGULATION MICROFILTRATION HYBRID SYSTEM FOR DRINKING WATER TREATMENT

Submitted by:
Sara Sadreddini

SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING

Thesis presented to the Nanyang Technological University
in fulfillment of the requirement for the degree of
Masters of Engineering by Research in Environmental Engineering
Singapore, 2008/2009

ABSTRACT

Coagulation combined with microfiltration has been receiving a great attention and has been evolving in recent years as an alternative for surface water treatment. There exists influential advantages with the novel hybrid system compared to other methods. Conventional surface water treatment plants include large flocculation and coagulation basins, which increase capital cost. Water treatment plants running with Nanofiltration (NF) and Reverse Osmosis (RO) can be costly to operate and also face with serious fouling problems. The proposed hybrid process with microfiltration offers a decentralized operating plant with a notable Natural Organic Matters (NOM) removal performance, minimized sludge, and mitigated fouling problem. All these factors signify great potential in integrating coagulation and microfiltration into one single process.

Since fouling is still the major problematic issue in this process, this research aimed to study on the membrane fouling behavior of humic acid (HA) as chemical model. Aggregates composed of alum as a coagulant and HA forming cake layer on the membrane decrease pore blockage but creates high resistance of deposited cake layer. However, cake layer can be easily backwashed. Therefore, aggregates size and structure control was found to be a strategic performance factor. Hence, morphological parameters of aggregates after coagulation were investigated along with microfiltration fouling behavior employing different analytical and imaging techniques. Static Light Scattering, UV-Spectroscopy, Inductively Coupled Plasma (ICP-OES), and 2D & 3D Imaging Analysis were applied.

Alum concentration of 40 mg/L for the synthetic feed water solution obtained as the optimum coagulant dose. High removal efficiency of HA (95%) and also residual Al^{+3} removal of 97.5% was achieved which meets the WHO guideline that suggests 0.2 mg/L of Al^{+3} for drinking water.

Coagulation pretreatment for microfiltration process was found to be useful for mitigation of fouling phenomena. Different coagulation mechanisms which leads to form different aggregate structures that consequently showed different aggregate fouling performances was investigated.

ACKNOWLEDGMENT

The completion of this thesis would definitely not be possible without the help, support and motivation of several important individuals and institutions.

First and foremost, I would like to thank my supervisor, Prof Darren D. Sun, for his encouragement, guidance, and openness, and also his critical comments that enriched the content of this work throughout the study.

I would like to acknowledge Agency for Science, Technology and Research (A*STAR) for providing the IGS two-year full scholarship to pursue my Master's degree.

Thanks to our research group for their help and inspiration especially Dr. Lee Pei Fung, and Mr. Alan Du.

A special thanks to Ms. Karina Listiarini for her wise advices and the effort dedicated to cooperate in conducting experiments and fruitful discussions to move this work in the right direction.

Thanks to the staff of Environmental Laboratory for their kind assistance.

And last but not least, many thanks to my family for their immense love and support.

PUBLICATIONS

S. Sadreddini, K. Listiarini, D.D. Sun and J.O. Leckie, (Nanyang Technological University, Stanford University) ‘Investigation of Fouling in Microfiltration for a Hybrid Coagulation-Microfiltration Process’, YWT-SIWW Singapore International Water Week, Poster Presentation, Singapore, June 2008.

K. Listiarini, **S. Sadreddini**, D.D. Sun and J.O. Leckie, (Nanyang Technological University, Stanford University) ‘Organic fouling of Nanofiltration Membranes: Force Measurements of Organic Foulants in Systems Containing Coagulant and Divalent Cations’, IWA World Water Congress and Exhibition, Oral Presentation, Vienna, September 2008.

TABLE OF CONTENTS

ABSTRACT

ACKNOWLEDGMENT

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1 INTRODUCTION	1
1. 1 Background	1
1. 2 History and Evolution of Membrane Treatment	3
1. 3 Research Objectives	4
1. 4 Research Approach	5
1. 5 Thesis Layout	6
CHAPTER 2 LITERATURE REVIEW	7
2. 1 Drinking Water Treatment and Membranes	8
2. 2 Membrane Fouling	9
2. 3 Coagulation	15
2. 4 Characterization	24
2. 5 Governing Theories in the System and Equations	24
2. 6 Background on Techniques	30
2.6. 1 UV-Spectroscopy	30
2.6. 2 Static Light Scattering Method	31
2.6. 3 Inductively Coupled Plasma Spectroscopy (ICP-OES)	33
2.6. 4 Optical Microscope	33
2.6. 5 Confocal Laser Scanning Microscope	34

CHAPTER 3 MATERIALS AND METHODS	37
3.4. 1 Preparations	40
3.4. 2 Jar Testing	42
3.4. 3 Dead-end Microfiltration Set-up	42
CHAPTER 4 CHARACTERIZATION OF AGGREGATES	45
4. 1 Effect of Alum Concentration on the Removal of HA	45
4. 2 Aggregate Size and Fractal Dimension Determination	47
4. 3 Imaging Analysis	57
4.3. 1 Optical Microscope Imaging	57
4.3. 2 Confocal Laser Scanning Microscope	59
CHAPTER 5 MICROFILTRATION BEHAVIOR	60
5. 1 Long-term Dead-End filtration behavior	61
5. 2 Membrane Resistance Dependence on TMP	65
5. 3 Sequential Batch Experiment	69
CHAPTER 6 EVALUATION OF COAGULATION-MICROFILTRATION PROCESS	69
6. 1 Effect of Alum Concentration on HA Removal	73
6. 2 Mass Balance	75
6. 3 Characterization of Aggregates	79
6. 4 Microfiltration Results	81

6.4. 1 Permeate Flux Decline Trends	81
6.4. 2 Total Resistance & Specific Cake Resistance results	83
 CHAPTER 7 CONCLUSION AND RECOMMENDATIONS	 86
 7. 1 Conclusions	 87
7. 2 Further Perspectives and Recommendations	89
 REFERENCES	 86

LIST OF TABLES

Table 3. 1	Specifications of the applied synthetic water	37
Table 3. 2	Chemicals used in experiment	38
Table 3. 3	Specifications of MF membrane	38
Table 3. 4	Equipments applied for the experiments	39
Table 3. 5	Specifications of bench scale MF set-up	44
Table 6. 1	Experimental protocol	71
Table 6. 2	Al concentration in different stage1.1s of process	77

LIST OF FIGURES

Figure 2. 1	Typical HA Molecule (Croue et al., 1999; Thurman, 1985)	11
Figure 2. 2	Schematic diagram of the PDFM system.	15
Figure 2. 3	Conceptual View of Coagulation Reactions	16
Figure 2. 4	Experimental solubility data for dissolved aluminum in solution. T=20-25°C. Dotted line is the theoretical solubility of aluminum in equilibrium with $\text{Al}(\text{OH})_{3(\text{am})}$ ($\text{pK}_{\infty} = 31.5$). (MWH, 2005)	18
Figure 2. 5	Schematic diagram of coagulation mechanism of aggregates.	20
Figure 2. 6	Relationship between specific cake resistance, floc size, and fractal dimension, based on modified Carman-Kozeny relationship (Guan and Amal et al., 2001)	29
Figure 2. 7	Cakes formed from the deposition of fluorescent latex aggregates (Park, 2006).	35
Figure 3. 1	SEM image of Millipore image of 0.2 μm MF Cellulose Acetate membranes fabricated as layers of random network of filaments. Pores are formed from the spaces between adjacent and overlapping fibers (Image provided by ADVANTEC)	39
Figure 3. 2	MF membrane bench-scale set-up connected to the pressurized nitrogen vessel	43
Figure 4. 1	Coagulated sample absorbance vs. alum concentration at $\lambda=254$	46
Figure 4. 2	Malvern mastersizer equipment, inlet and outlet piping from the laser chamber(t=0 min). a) the blue dye was seen only in inlet (t=4 min). b) Light blue was seen in outlet. c) dark blue was seen in outlet (t=8 min).	48
Figure 4. 3	Continues trials for $D(0.5)$ measurement of 20 mg/L HA and 40 mg/L alum for 6 hours.	49

Figure 4. 4	D(0.5) of Aggregates before filtration vs. iteration time for different concentrations of alum. D(0.5) to stay at a fixed value after 30 min.	51
Figure 4. 5	D(0.5) of Aggregates after filtration vs. iteration time for different concentrations of alum.	51
Figure 4. 6	D(0.5) vs. alum concentration for aggregates before and after filtration.	52
Figure 4. 7	Scattering Plot for D_f calculation	54
Figure 4. 8	Fractal Dimension (D_f) of aggregates before filtration vs. iteration time recorded for different concentrations of alum.	55
Figure 4. 9	Fractal dimension (D_f) of aggregates after filtration vs. iteration time recorded for different concentrations of alum.	55
Figure 4. 10	Fractal Dimension (D_f) vs. alum concentration for aggregates before and after filtration.	57
Figure 4. 11	A single aggregate after coagulation taken by Optical Microscope. Aggregate made up of HA (20mg/L)+alum (40 mg/L)	58
Figure 5. 1	Flux decline vs. time fitted to experimental data. 20 mg/L HA+ 40 mg/L alum, at 20 kPa, membrane: 0.2 μ m cellulose acetate.	63
Figure 5. 2	(a) Fitted flux vs. time, (b) Standard 1 st derivative of the model vs. filtration time	64
Figure 5. 3	Loose aggregates accumulating on the membrane surface and forming cake layer inside of the MF cell.	64
Figure 5. 4	Effect of TMP on membrane resistance. Membrane is MF type cellulose acetate 0.2 μ m.	67
Figure 5. 5	Flux behavior of DI water filtration during the operation time.	68
Figure 5. 6	Reversibility test at 20 kPa & 100 kPa.	68
Figure 5. 7	Total membrane resistance of sequential batch dead-end filtration	69
Figure 6. 1	Experimental protocol explained for the complete set of experiments	72

Figure 6. 2	Calibration curve for humic acid stock solution (HA)	73
Figure 6. 3	UV removal rate for a range of alum concentration. pH=7, ionic strength=10mM.	74
Figure 6. 4	HA concentration removal for a range of alum concentration. pH=7, ionic strength=10mM.	75
Figure 6. 5	Aluminum concentration for a range of alum concentration. pH=7, ionic strength=10mM.	76
Figure 6. 6	Aluminum removal percentage for a range of alum concentration. pH=7 & ionic strength=10mM	78
Figure 6. 7	Sodium concentration for a range of alum concentration. pH=7, ionic strength=10mM	79
Figure 6. 8	Size of aggregate for a range of samples (20-100 mg/L) formed of different alum concentration.	80
Figure 6. 9	Permeate flux of microfiltration vs. time. 50 mL of coagulated feed in a range of alum concentrations was filtered (TMP=20 kPa).	82
Figure 6. 10	Permeate flux of microfiltration vs. time. 50 mL of coagulated feed in a range of alum concentrations was filtered (TMP=100 kPa).	83
Figure 6. 11	Variation of Specific Cake Resistance as a function of alum.	84
Figure 6. 12	[HA]/[Al] deposited on the cake layer for a range of concentration on alum	90

CHAPTER 1 INTRODUCTION

1. 1 Background

Water is enormously spread on the earth. However, 97% of the world's total water is seawater. Of the remaining fresh water, two-thirds of this fresh water is locked in glaciers, ice or snow, leaving only one percent of the world's total water available for direct human consumption. Presently, there is a greater demand than ever before for safe drinking water throughout the entire world (MWH, 2005) and ever-tightening regulations on the quality of water is increasing as well. Therefore, governments around the world are setting aside a significant budget in the area of water treatment and reuse, hoping of creating improved technologies to increase the economical and operational efficiencies of present water treatment technologies.

Removal of natural organic matters (NOM) is critical to meet water regulations on chlorinated organic compounds such as trihalomethanes (THM) which has been known as toxic byproducts resulting from the chlorination and disinfection of residual organic compounds. Furthermore, the existence of pesticides, herbicides, and other agrochemicals occurring in surface water arise health concerns in current water treatment technologies. Therefore, there is driving need to improve these technologies and create effective solutions for NOM removal.

Currently, there are many combinations of physical and chemical methods available in the industry for water treatment. The use of activated carbon, chlorination, ozonation, UV-radiation, coagulation/flocculation, sand filtration, and membrane technologies. Some of these conventional technologies such as activated carbon, coagulation/flocculation, and sand filtration only separate the contaminants to solid

forms for disposal. High cost of ozonation has restricted this method from being widely employed. Plus, formation of bromate is a critical issue for O_3 treatment using O_3 dose of more than 4 mg/L (kim et al., 2009).

Novel membrane technologies such as nanofiltration (NF) combined with photocatalytic reactors has been evolved in recent years (Molinari et al., 2002), but the high operation and maintenance costs of the plants are still a considerable issue. However, technologies such as reverse osmosis (RO), ultrafiltration (UF) and microfiltration (MF) offer efficient and cost effective choice for producing portable water from raw water. Fine colloids and natural organic matters can be removed particularly with these methods.

Although membrane technologies are widely accepted solution for portable water production, the existence of contaminants such as particulates, suspended solids, colloids, bacteria and non-biodegradable organic compounds in the raw water creates primary limitations in fouling problem on the surface of the membrane. Humic acid constituents as one of the main compounds of NOMs are known as one of the major foulants in water (AWWA, 2005).

Previous studies have shown that the combination of two processes of coagulation and membrane is a beneficial chemical-physical technique to mitigate the fouling problem in membrane systems. Coagulation process agglomerates and adsorbs particulate matters together as aggregates or flocs. The loose flocs can be easily removed from the surface of the membrane.

Microfiltration is the most cost effective membrane filtration method among the other membrane technologies that makes this combined process economically acceptable. The size of the plant reduces significantly as the coagulant can be injected to the feed water prior to microfiltration. Therefore there is no need for huge

coagulation/flocculation basins. In this process aggregates after formation are filtered through the membrane therefore there is no need for sedimentation basins as well. Plus, the sludge disposal is improved in this process in view of the fact that aggregates are dewatered at microfiltration operating pressure.

The control of this system in order to achieve the optimum performance needs careful study. A wide range of physical and chemical factors delicately needs to be controlled. In this regard knowing the process, nature and formation mechanism of flocs is necessary. Different mechanisms of coagulation can affect contaminant removal performance and also fouling mitigation yield. Studies have been carried out to optimize and design this system mainly for surface waters (Carrol et al., 2000; Zhang et al., 2005; Lerch et al., 2005). However there are few evolution studies addressing the correlation of the nature of organic compounds to the fouling performance of this system.

Considering this, a fundamental direction of this research involves development of a hybrid coagulation membrane system to simulate the integrated process.

1. 2 History and Evolution of Membrane Treatment

Since the early 1990's, there has been rapid growth in the use of low-pressure membranes comprising microfiltration and ultrafiltration for the production of drinking water. The process has received a great deal of attention, and in many ways, it is a sustainable, and reliable treatment technology used on a variety of scales around the world. In the United States alone, the growing demand for membrane treatment technology such as reverse osmosis RO, microfiltration and ultrafiltration, in all water treatment applications rose 6.5 percent annually starting in 1994, reaching \$305 million in the year 2001 (Vial and Doussau, 2002), and considerable further growth has been

seen since then. The process provides water treatment through physicochemical separation techniques that use differences in permeability and physical blocking of the water constituents as a separation mechanism. Conceptually, membrane treatment is a reasonably simple technology that achieves high standards of treatment in the long run. Major hindering factor for membrane uses are due to high capital costs, although in recent years the cost of membrane systems has decreased substantially. Laine *et al.* (2000) reported that between 1992 and 2000, 50% decline in costs occurred in membrane market. This decrease in costs has been mainly attributed to two factors: an increase in membrane surface area per module and an increase in mass production of these membrane modules. As a result of the costs decline, the use of these systems become a very attractive and feasible alternative to conventional drinking water treatment over the past 20 years.

1. 3 Research Objectives

The primary goal of this research was to investigate the effectiveness of chemical coagulation conditions as a pretreatment to microfiltration polymer membranes for mitigation of fouling caused by natural organic matter.

The following is a list of specific objectives:

- Optimize coagulation by determining suitable coagulant doses to remove humic acid as the representative of NOM in surface water prior to being treated by the MF membrane.
- Study the dead-end filtration process of membrane.
- Investigate the morphology of the aggregates formed of HA and alum by different techniques (Imaging Analysis, Static Light Scattering)

- Develop a laboratory scale setup in which coagulation is incorporated with a dead-end MF membrane.
- Correlate the aggregate morphology to MF performance

1. 4 Research Approach

After an extensive literature review was completed, the experiments was divided into three main parts:

Part I: The coagulation of synthetic water containing a specified amount of NOM in the form of humic acid was carried out. Jar test and characterizations (2D and 3D Imaging, Light Scattering) were carried out as well.

Part II This part involved experiments to study the flux decline behavior and membrane resistance development. A flow pattern of long-time dead-end filtration for coagulation-MF system was obtained experimentally and modeled subsequently. A specific experimental protocol was used to measure different membrane resistances including cake layer (R_{cake}), pore blocking (R_{pore}) and membrane surface (R_{mem}) resistances. In this part the major causes of fouling was found (reversible & irreversible).

Phase III Subsequent to experiments on coagulation process and microfiltration process, and after getting familiar with the nature of flocs (aggregates) and main controlling parameters for each process, for the last batch of experiments, a complete series of experiments including coagulation and microfiltration were carried out for the same synthetic feed water. After analytical measurements, mass balance calculation was applied to find all the concentrations of elements consisting of Al^{+3} , NA^{+} and species to further investigate the nature of the flocs.

1. 5 Thesis Layout

This report is organized in 7 chapters:

Chapter 1, as an introduction to this research work, comprises of a summary of the research purpose on surface water treatment for drinking water usage and also the scope of the work in this thesis. Chapter 2 presents background information on main pollutants in drinking water treatment, coagulation and microfiltration process and the combination of the two processes in order to remove the pollutants, the history, pros and cons, and major problems. A literature review was also done on the methodologies and the principle of techniques that were applied in this project. Chapter 3 comprises information on materials and methodologies and experimental design applied in this research.

The subsequent chapters provide experiment results. Chapter 4 mainly presents the results of jar test and characterizations of aggregates after coagulation process. Characterization techniques that were used are: static light scattering, UV-spectroscopy, image capturing of aggregates by optical and confocal laser scanning microscopy. Chapter 5 contains results of dead-end microfiltration. Flux behavior and flux data conceded membrane resistances is produced. The effect of trans membrane pressure (TMP) on fouling was examined in this part as well. A set of sequential batches of experiments was carried out to observe for reversibility on tests in the combined coagulation-microfiltration process. Chapter 6 contains detailed results of complete sets of experimental design followed by characterization and concentration measurements. The main goal of this part is to correlate the aggregate (or floc) size and characteristics to microfiltration performance and fouling mitigation.

Chapters 7, as the final chapter includes conclusions and recommendations. It

summarises the results and corresponding analysis. The principal conclusions and recommendations are laid out in this chapter as well. The subsequent section contains a complete reference list for all sourced information in the thesis.

CHAPTER 2 LITERATURE REVIEW

A background review on the use of membranes as a novel emerging method for drinking water treatment is described as an introductory for this chapter. Subsequently, the major membrane organic compound (foulant) that was used in synthetic water in this work (Natural Organic Mater) is explained. Next, a review on microfiltration, and coagulation pretreatment, and then a combination of the two procedures are presented. At the end, the background and information about the techniques used in this work are discussed.

2. 1 Drinking Water Treatment and Membranes

Micro-sized porous membranes were firstly patented in the 1920's (Belfort et al., 1994). They were limited primarily to laboratory use until the 1950's. Initially, they were used for enumerating bacteria, removing microorganisms and particles from liquid and gas streams, and fractioning and sizing macro-molecules such as proteins (MWH, 2005). In the 1950's industries began incorporating membrane filtration, primarily for the sterilization of liquid pharmaceuticals and intravenous solutions. Membrane filtration also slowly began to be used for industrial waste treatment, in order to separate oils, fats, acids and brine.

Microfiltration and also ultrafiltration systems are particulate filters and unlike nanofiltration and reverse osmosis do not remove dissolved constituents. This makes them more suitable for use as a replacement to conventional filters. MF mainly removes particulate matter and turbidity as well as larger microorganisms and viruses. The cost of low pressure membrane systems is a major driver for increased membrane

application compared with conventional treatment technologies as well. Every year, the capital cost of MF and UF systems has decreased as economies of scale and a competitive market force innovative developments. Generally, low pressure membrane facilities are one half to one third the cost of an NF or RO facility (Farahbakhsh et al., 2004). In addition, implementing backwashing or cleaning strategies has reduced operational cost, by reducing the degree of fouling that occurs on the surface and inside the pores of the membranes.

One factor that empowers the applicability of membranes is their operational flexibility. These systems can be used in conjunction with other treatment processes to achieve additional removal. There are several pre-treatment techniques available to use in combination with a MF or UF membrane: pre-filtration, pH adjustment, coagulation, bio-filtration adsorption and pre-oxidation (Kimura et al., 2005).

The main drawback of using membranes is the fouling problem. Fouling phenomena occurs in all types of membranes including MF. Tackling with fouling is needed and a lot of research work focus on it.

2. 2 Membrane Fouling

Deposition of colloidal materials on the membrane surface may block membrane pores and/or create an additional layer of resistance to permeation. Losses in permeate flux are operationally referred to fouling.

Pore blocking is internal fouling that essentially results in a decrease of the membrane porosity (R_{pore}) and an increase in resistance (R_{total}). It is caused by adsorption of dissolved matter or bulk phase particles that are small enough to enter the membrane pores and deposit on their surface. If incompressibility of the particles is

assumed, it equals the density of the bulk particles. Pore blocking is considered as irreversible fouling and might be removed by chemical cleaning, not physical cleaning (Lee et al., 2000).

The particles retained on the membrane surface or attach to the membrane, contribute to cake layer formation and resistance (R_{cake}), or they return to the bulk phase.

Membrane fouling can be reversible and irreversible. Irreversible adsorption produces a long-term flux decline that cannot be fully recovered by hydraulically cleaning the membrane (Jones et. al, 2000). It is created within a short time and at the initial stage of filtration cycle, and then is stabilized over a long period. The stabilization of the flux takes place at a considerably lower level than the initial one (Konieczny, 2002). Reversible fouling can be removed by backwashing. Microfiltration systems must be backwashed at the right moment to regenerate membrane and put it in operation.

2.2. 1 Major Fouling Source in Microfiltration: Natural Organic Matters

One of the important groups of substances that exist in surface and ground waters are NOMs, found in concentrations ranging from 1 to 15 mg/L, depending on the season and specific location (AWWA, 2005). Ground water sources in North America tend to have less than 2 mg/L TOC, while rivers tend to have more elevated levels ranging from 3-6 mg/L.

Humic substances are major components of suspended and dissolved NOM in aquatic environments. Decomposition matter of plant and animal mainly produce humic substances in soil constitutes. Based on basic biological processes, carbon is recirculated to the atmosphere as carbon dioxide and associated elements (nitrogen,

phosphorous, sulfur, and various micronutrients) appear in forms required by higher plants. In the process, some of the carbon is assimilated into microbial tissues (i.e., the soil biomass); part is converted into stable humus.

A large amount of humic molecules are represented by hydrophobic compounds (long alkyl-chain alkanes, alkenes, fatty acids, sterols, and phenyl-alkyl residues of lignin degradation) which allow their self-association into macromolecular structures separated from the water medium. They have both aromatic and aliphatic components, allowing them to be surface active, which is the ability of a compound to lower the surface tension of a given medium in which it is dissolved (Kokkola et al., 2006).

Humic substances as well as polysaccharides and proteins have been shown to exert fouling in membrane process. Humic acid is one of the major components of humic substances. Humic substances make up a large portion of the dark matter in humus and are complex colloidal macromolecular mixtures that have never been separated into pure components (Piccolo, 2001). Figure 2. 1 highlights some of functional groups of humic acid molecule (Croue, et al., 1999; Thurman, 1985).

Figure 2. 1 Typical HA Molecule (Croue et al., 1999; Thurman, 1985)

Removing NOM is an important objective in many treatment facilities because of its effect on treatment processes and finished water quality. NOM can decrease effectiveness of activated carbon, increase chemical doses, and is an essential factor in formation of disinfection by-products. It also has a dramatic impact on membrane fouling.

In this work, humic acid was used for the synthetic feed water in all the tests. The experimental protocol for the preparation of synthetic water is explained in the next chapter.

2.2. 2 Some Approaches for Microfiltration Fouling Reduction

In recent years, many scientists have focused on different methods to minimize microfiltration fouling. A brief literature review of the research work in this regard is presented as follows:

Ultrasound on MF cross-flow set up was proposed as another novel method for MF fouling reduction. Ultrasound increases the flux by breaking the concentration polarization and cake layer at the membrane surface. The drawback of this method is membrane erosion (Kyllonen, Pirkonen et al. 2005; Chen, Weavers et al. 2006). Masselin (2001) also studied the effect of ultrasound irradiation at a frequency of 45 kHz on different polymeric membrane materials for 2 hours. It was observed that polyethersulphone was affected by irradiation over its entire surface, but the polyvinylidene fluoride and hydrophilic polyacrylonitrile membranes presented no significant change.

Ceramics materials have gained popularity, but have not grown to be as popular as the polymer-based modules. Normally Ceramic membranes exhibit excellent tolerance to pH extremes and oxidants as well as high mechanical strength. Lee and Cho (2004) initiate the use of an inorganic ceramic membrane for water treatment (especially NOM removal) suggested some ways of replacing polymeric membranes in drinking water plants, by identifying the advantages offered by ceramic membranes.

A membrane vibration method was proposed to reduce fouling of carbon loaded wastewater plant. As a result, the increase in trans-membrane pressure, temperature and vibration amplitude leads to the increase in the permeate flux (Choi and Dempsey , 2004).

Amongst all novel technologies, coagulation as the pretreatment stage for microfiltration was reported a useful technique for treating particles in water, including NOM (Kim and Hong et al., 2006; Peuchot and Benaim, 1992).

Lee (2000) stated that by applying coagulation before MF the TOC removal efficiency increase from 10% to 15-25%. The highest removal of TOC occurred at the charge neutralization condition because organic substances become less electronegatively charged at lower pH and thus subject to be easily coagulated.

In another recent study Konieczny (2006) claimed 100% removal for TOC for this hybrid system. These studies involved synthetic water containing humic acids in concentrations of 30 and 40 mg/L in unit processes of coagulation, microfiltration, and the hybrid process coagulation–sedimentation–microfiltration.

Howe and Clark (2006) conducted a study to further understand the effect of pre-coagulation. Their primary objective was to evaluate the effect of coagulant type, its

dose, and application conditions on membrane performance. Five different natural surface waters were used, coupled with three different membrane materials. After all of the results were combined, it was concluded that coagulant dose was the most significant factor in determining the severity of fouling. At low doses, the membrane fouling was worse when compared with no coagulant. These doses were generally coupled with minimal floc formation.

Zhang (2005) also applied this system for fluoride removal from drinking water and used aluminum salt as a coagulant. As a result the concentration of fluoride was reduced from 4.0 mg/L in raw water to less than 1.0 mg/L in finished water, and the concentration of residual aluminum in finished water was not more than 0.05 mg/L.

Kim (2006) studied on different types of mixing in coagulation in a hybrid system. He examined Pump Diffusion Flash Mixing (PDFM) and Conventional Rapid Mixing (CRM). PDFM is in-line mixing as shown in *Figure 2. 2*, for quick dispersion of hydrolyzing coagulant, which also has the potential to solve problems such as the noise, high energy consumption and high maintenance cost, associated with the use of mechanical mixers. CRM is a back-mixing method consists of a square baffled container, with a six flat-bladed turbine impeller of one-third the standard geometry, similar to that of a turbine impeller used in a real plant for drinking water production. Results of the tests showed that CRM type of mixing is more effective in the reduction of fouling due to residual NOM compared with PDFM.

Figure 2. 2 Schematic diagram of the PDFM system.

2. 3 Coagulation

Coagulation is an integral unit operation in most water treatment plants. This combined process consists of both chemical and physical separation steps. It is used to destabilize suspended particles, heavy metals and react with dissolved organic material in the raw water. Proper coagulation is essential for good filtration performance as well as disinfection byproduct control. Optimizing coagulation is the most cost-effective way to decrease treated water turbidity and disinfection byproduct levels.

Four mechanism of enmeshment, adsorption, charge neutralization/destabilization, and complexation/precipitation occur for removal of natural organic matters and colloidal particles in drinking water. *Figure 2. 3* illustrates coagulation reactions.

Figure 2. 3 Conceptual View of Coagulation Reactions

Different coagulant materials can be used in water treatment plants. For NOM removal mostly aluminum salts (normally alum, $\text{Al}_2(\text{SO}_4)_3$) or PACls are used. PACls have similar chemistry to alum, except that PACls contain highly charged polymeric aluminum species as well as monomers (i.e. $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$). PACls can be used at higher pH values without resulting in elevated dissolved Al levels. Due to the presence of the Al_{13} polymer, the surface charge on PACl floc has a larger positive charge density than alum floc.

Fe-based salts (e.g. FeCl_3) can also be used in coagulation. Overall solubility of Fe(III) is less compared to Al(III). This means that Fe-based coagulants can be used over a much greater pH range than Al-based coagulants without worrying about dissolved metals concentrations in the finished water.

Coagulation is conventionally followed by sedimentation to achieve solid-liquid separation, but in this system there is no sedimentation basin, therefore all aggregates are sent to the next step, which is microfiltration. In this research alum was used as a coagulant. Therefore coagulation mechanism of alum is explained in detail in this report.

2.3. 1 Coagulation Mechanism of Alum

In order to investigate the overall mechanism of the process, it is necessary to be familiar with the coagulation mechanism. Aluminum is the most widely used coagulant (Dentel and Gossett 1988) and it is been used in this research work.

Under water treatment conditions, alum chemistry can be described by the presence of three species: Al^{+3} , $\text{Al}(\text{OH})^{+2}$, and $\text{Al}(\text{OH})_4^-$ in equilibrium with an amorphous $\text{Al}(\text{OH})_{3(\text{am})}$ solid phase (Hayden and Rubin 1974; Van Benschoten and Edzwald 1990). The distribution of the species vs. pH is shown in Figure 2. 3. The figure shows the standard diagram for the aluminum ion. It shows that the operating range for aluminum hydroxide precipitation is in a pH range of 5.5 to 7. Alum is least soluble at pH 6. This means that at pH 6, the maximum amount of coagulant is converted to solid phase aggregates (MWH, 2005).

Figure 2. 4 Experimental solubility data for dissolved aluminum in solution. $T=20-25^{\circ}\text{C}$. Dotted line is the theoretical solubility of aluminum in equilibrium with $\text{Al}(\text{OH})_{3(\text{am})}$ ($\text{pK}_{\infty} = 31.5$). (MWH, 2005)

The coagulation mechanism generally involves either charge neutralization or precipitation by positively charged coagulant species or enmeshment in or adsorption on the surface of precipitated aggregates. The two main ways in which hydrolyzing coagulants act to remove particles are charge neutralization and sweep flocculation. Charge neutralization is a reasonably simple mechanism, which involves the specific adsorption of the cationic hydrolysis products from solution onto the negatively charged particles. NOM and other particles can be destabilized by small amounts of hydrolyzing coagulant. It is important to note that larger amounts of the positively charged coagulants (over dosing) can cause charge reversal, leaving the particles positively charged and thus re-stabilized. When charge neutralization is the dominant mechanism, the coagulant dose is generally considered to be proportional to the concentration of particles in solution, although in some cases, required doses can still be dominated by the type of NOM found in the water.

In some cases it is found that a higher coagulant dose is more effective, due to extensive hydroxide precipitation and the process known as sweep flocculation (Jiang, 2001). Sweep flocculation can overcome two of the primary disadvantages of destabilization by charge neutralization: The first being the fact that very accurate control of the coagulant dose is required to give optimum destabilization, and the second is the fact that the coagulation rate depends on the particle concentration, and can therefore be extremely low for dilute solutions. Sweep flocculation avoids both of these problems by using much higher doses, forming larger quantities of amorphous hydroxide precipitates. The target particles are enmeshed in this growing precipitate, and then can be removed by sedimentation, giving the term “sweep floc”. Sweep floc is the mechanism that takes place when the water pH is above the point of zero charge for the dissolved species formed from the coagulants such as alum.

In solution small Al^{+3} ions form bonds with oxygen atoms of six surrounding water molecules of $\text{Al}(\text{H}_2\text{O})_6^{+3}$. The hydrogen-oxygen bond is subsequently weakened, and the hydrogen ions are released into solution. This reaction is known as hydration. The process is a progressive de-protonation of water molecules. Hydrolysis of ions is generally represented as a sequential replacement of the water molecules by hydroxyl ions (Richens, 1997). A simple way to represent this dynamic process for Al^{+3} is as follows:

Figure 2. 5 illustrates the schematic diagram of two coagulation mechanisms of charge neutralization and sweep flocculation.

Figure 2. 5 Schematic diagram of coagulation mechanism of aggregates.

NOM is generally suspected to be removed through colloidal destabilization and charge neutralization (Randtke, 1988). In this work both mechanisms are investigated and the NOM removal percentage during the process are determined.

It should be noted that presence of anions such as HCO^- , SO_4^{3-} and silica acid causes profound effects on aluminum precipitation and modifies the charge properties of colloids (Letterman and Vanderbrook, 1983; Amirthamjah and O'Melia, 1990; Duan and Gregory, 1998).

2.3. 2 Coagulant Dose

Selection of optimal coagulant dose and formation of aggregates to gain appropriate physical and chemical properties in the coagulation process are essential for efficient particle removal in water treatment plants (Ramaley, 1981; O'Melia, 1985; Wiesner, 1987).

Optimum values of coagulants are different in coagulation process compared to coagulation-microfiltration. Alum dose of 5.7 mg/L at pH 7, and 5.5 mg/L at pH 6 was reported as the optimum values in coagulation process which leads to 82% and 74.4% TOC removal for 7 mg TOC /L for alum salt respectively. (McDonogh and Fell et al., 1984).

Duan (2002) found the optimal coagulation range for humic acid at approximately pH 6 and an aluminum concentration corresponding to super-saturation with respect to amorphous aluminum hydroxide precipitate. At this range a strong charge neutralization effect of the seawater humic acid solution was observed.

In another study ferric salts were used as a coagulant (Duan and Graham et al., 2003). Overall results indicate that neither the degree of charge neutralization, nor maximum floc size, as single parameters are adequate to describe the extent of dissolved humic acid removal during the coagulation. At 21.4 mg/L of FeCl_3 , larger and stronger floc formation corresponding to a very low ratio of $[\text{OH}]/[\text{Fe}]$ occurred. It is speculated that with pre-coagulation pH adjustment to pH 6, more ferric ions/ferric hydrolysis species can directly interact with humic acid, rather than with OH^- , leading to a greater co-precipitation of humic acid molecules. It is believed that there may be a significant competition between the process of ferric ion hydrolysis and interactions between

intermediate Fe-hydrolysis species and humic acid molecules, giving a co-precipitation process.

2.3. 3 Effect of Water Chemistry on Coagulation Performance

The right value of pH at which coagulation occurs is a very important parameter for proper coagulation performance because it affects the surface charge of colloids existing in water, charge of all dissolved water species (carbonate, acids, NOM functional groups, etc.), charge of dissolved phase coagulant species, surface charge of floc particles, and coagulant chemistry as well.

Charge neutralization effect of humic substance and hydrolyzing metals in water solution usually occurs at acidic pH (4.5–6). This value may correspond an optimum pH of organics removal. Bernhardt and Schell (1993) reported that optimal coagulation effects occurred at dosages where the point of zero charge was reached after addition of metal coagulants in natural colored waters in the same range of pH. However, this may not be necessarily true specifically for humic acid solution. In another study the effect of water chemistry was studied on surface freshwater and seawater (Duan et al., 2002). The experimental results showed that the coagulation of humic substances in seawater has distinctly different characteristics compared to the well-established coagulation behavior in surface freshwaters. These differences can be attributed to the solution chemistry and its modification of the aluminum hydrolysis reactions and the nature of the precipitates formed. In fact, insolubility of calcium and magnesium salts varied with pH. Although it was complex to predict the exact resulting interactions between the precipitating species (calcium and magnesium salts) in seawater and humic substances, the overall effects of enhanced precipitation of aluminum at the high pH (8-10) for freshwater and lower pH (4-8) for seawater on coagulation of humic acid was significant.

Solution chemistry affects on the rate and extent of compound's adsorption as well. Jones and O'Melia (2000) studied this effect on the rate and extent of a protein (BSA) representative of compact, stable material as well as humic acid (from Suwannee river) representative of flexible, heterogeneous material adsorption onto a regenerated cellulose ultrafiltration membrane. Isotherms were performed to determine equilibrium adsorption behavior. Rate of adsorption was determined by measuring adsorbed mass as a function of time. Experiments showed adsorption of both protein and humic acid was higher at lower pH values. Increased salt concentration on the other hand, reduced electrostatic repulsion between like-charged material (increasing adsorption) and decreased electrostatic attraction between oppositely charged material (decreasing adsorption).

McDonogh (1984) found the values of permeability predicted from double layer theory mirror experimental trends with zeta potential and are in good agreement with experimental values, suggesting that the double layer approach can be used to model the hydraulics of retained colloid layers. In contrary, Duan (2003) claimed that zeta potential can only act as an approximate reference for predicting the performance of coagulation in terms of dissolved organics removal, but cannot serve as the sole indicator for such monitoring purposes. Results of the experiments showed the greatest humic acid removal corresponded to the lowest zeta potential.

In this work, to control the water chemistry, pH was adjusted at neutral, and ionic strength was controlled by adding NaCl and strong base (NaOH) and strong acid (HCl).

2. 4 Characterization

Aggregates that form as a result of the coagulation process can be described using the concepts of fractal geometry. Fractal scaling models have been developed to explain the aggregate size-density relationships, aggregate settling velocity, porosity, and permeability (Meakin, 1988). However, some experimental results showed that for the low range of fractal dimension the cake porosity may hardly depend on the fractal dimension of aggregates, but for the region of higher values it may decrease with increasing of the fractal dimension (Park and Lee et al., 2006).

From a geometrical point of view the most peculiar feature of a fractal is its random spatial arrangement, tenuously filling the space and characterized by irregular ramifications that never allow it to fill the space in a dense manner. The essence of a fractal object is the repetition of randomness at all length scales or the repetition of structure within the structure. The most important parameter in fractal theory is the fractal dimension. In the general theory of fractals, the fractal dimension corresponds to the degree of irregularity and complexity or the space-filling capacity of an object. It can describe how an object occupies space. This can be used to characterize the compactness of an aggregate, with loose aggregate having a low fractal dimension and more compact aggregates having a higher fractal dimension. As the way the aggregate occupies space is being examined, it is a volume fractal dimension is measured. Fractal dimension can be defined in relation to changes in packing density, connectivity between component particles, tortuosity, surface area, and other characteristics of an object that are observed to follow a power law with scale (Jung and Amal et al., 1995).

2. 5 Governing Theories in the System and Equations

2.5. 1 Membrane Resistance calculation

The overall fouling mechanism can be described using the ‘resistance in series model’ that divides the total resistance of the membrane (R_{total}) into four primary components of resistance that contribute to membrane fouling: resistance due to the intrinsic membrane (R_{mem}), resistance due to cake formation (R_c), resistance due to internal pore fouling (R_p) and resistance due to adsorption effects (R_a) which, as obtained in preliminary experiments, is very small for MF microfiltration and can be neglected.

$$R_{total} = R_{mem} + R_c + R_p + R_a \quad Eq. 2. 1$$

In general, one of the parameters of special interest in applications of membrane filtration is the permeate flux which is governed by Darcy’s law. As explained, the trans-membrane pressure required to press the water through the membrane is proportional to the permeate flux:

$$J = \frac{\Delta P}{\eta R_{total}} \quad Eq. 2. 2$$

In order to measure the specific cake resistance of the membrane (α_c) filtration theory is applied (Coakley and Jones, 1956):

$$R_c = \alpha_c \frac{m_p}{A} \quad Eq. 2. 3$$

Where m_p is the mass of deposited particles, A the membrane area and α_c the specific cake resistance of the deposit.

Another method (Schippers et al., 1980) which has been used to calculate the specific

resistances of cake is ‘membrane fouling index’ (MFI) method. In this method the permeate volume (V) is measured as a function of filtration time (t) for various suspension and operating conditions. According to cake filtration theory *Eq. 2. 4* is obtained. Based on this equation, if t/V vs. V is plotted, from the slope of the line specific resistance of the cake (α) can be obtained where μ is viscosity of the medium, c is the concentration of the particles, A is the filtration area, ΔP corresponds to the trans-membrane pressure (TMP) are known parameters.

$$\frac{t}{V} = \alpha_c \frac{\mu c}{2A^2 \Delta P} V + \frac{\mu R_{mem}}{A \Delta P} \quad \text{Eq. 2. 4}$$

In this research work, specific cake resistance was obtained by both methods of resistance in series model and MFI. Not much difference was seen for the results in membrane cake resistance for both methods, therefore only the results of first method were reported in this thesis.

2.5. 2 Relationship of Aggregate Morphology and Membrane Resistances

For aggregated particles, the fractal dimension quantifies how the particles occupy the space in the aggregate. It preserves the fundamental dimension roles in the measurement where the Euclidean dimensions are used as exponents. For example, the mass of a fractal aggregate M, with fractal dimension D_f is proportional to aggregate size R, raised to power D_f :

$$M \propto R^{D_f} \quad \text{Eq. 2. 5}$$

Eq. 2.5 differs from an ordinary mass-size relationship only in that the power

coefficient D_f is no longer limited to an integer. In this system, the fractal dimension can be used to characterize changes in mass density of the aggregate, $\rho(R)$, observed within a sphere of radius R centered at some point in the aggregate:

$$\rho(R) \propto R^{D_f-3} \quad \text{Eq. 2. 6}$$

Where $1 \leq D_f \leq 3$ for an object in 3-dimensional Euclidean space. An entirely compact aggregate such as a coalesced sphere will have a $D_f=3$. Smaller fractal dimensions characterize aggregates with “open” configurations of particles. The concept of fractal dimensions is only properly defined when using an asymptotic limit to infinitely small lengths. However, when considering real objects, there always exist lower and upper size limits beyond which the objects are no longer fractal. In particular, when considering aggregates, the lower cutoff is the radius of the primary particle, while the upper size is the radius of gyration of the aggregate (Jung and Amal et al., 1995). It was reported that for compact aggregates, D_f was found to have values in the 2.3-2.5 range (or higher if “restructuring” occurs) while for “loose” aggregates, values in the 1.7-1.8 range are common (Lee and Fane et al., 2005). According to another study with hematite particles, D_f range is from 2.3 for rapid (diffusion limited) to 2.8 for slow (reaction limited) aggregation (Amal et al., 1990).

Porosity of aggregates (ϵ_a) in solution has been defined as a function of particle size R_o , the aggregate size R , and the fractal dimension D_f (Veerapeni and Wiesner 1996):

$$\epsilon_a = 1 - \left(\frac{R}{R_o}\right)^{D_f-3} \quad \text{Eq. 2. 7}$$

Another interpretation of porosity is defined by Carman-Kozeny relationship (Carman, 1938) which is called cake porosity ϵ_c . Specific cake resistance α_c is defined as a

function of cake porosity ϵ_c , particle size diameter R_o , and particle mass density ρ_p and K , Kozeny coefficient:

$$\alpha_c = \frac{36K(1 - \epsilon_c)^{D_f-3}}{\rho_p R_o^2 \epsilon_c^3} \quad \text{Eq. 2. 8}$$

Carman–Kozeny relationship recognized to be valid for media with porosities less than 0.5 (Veerapeni and Wienser 1996).

For small flocs, a Modified Carman-Kozeny relationship was determined examining biosolids by addition of cationic polymer from activated sludge wastewater treatment plant by (Guan, Amal et al. 2001) :

$$\alpha_c \propto \frac{1}{\left(\frac{R}{R_o}\right)^{3-D_f} \left(1 - \left(\frac{R}{R_o}\right)^{3-D_f}\right)^3} \quad \text{Eq. 2. 9}$$

According to this equation specific cake resistance increases with decreasing aggregate size R , and increasing fractal dimension D_f .

Conversely, effects of differences in floc size are most significant when flocs are more compact. Figure 2. 6 shows the cake resistance dependence on the floc size and shape.

Figure 2. 6 Relationship between specific cake resistance, floc size, and fractal dimension, based on modified Carman-Kozeny relationship (Guan and Amal et al., 2001)

2.5. 3 Background on Colloidal Membrane Filtration Modeling

Mathematical modeling of fouling mechanism is another approach to illustrate the fouling mechanism of colloids.

Inter-particle interactions and cake layer compression were modeled by Chen and Kim (2006). In another study (Duclos-Orsello, Li et al. 2006) pore blocking and cake layer formation during microfiltration were modeled. In this study, a model was developed accounting for three fouling mechanisms: pore blockage and cake filtration which represent external fouling, and pore constriction which represents the internal fouling neglected in the previous combined fouling model. The model predictions were validated by experimental results from polystyrene microsphere solution through PCTE

membranes (representing complete external fouling), prefiltered BSA solution through Durapore membranes (representing internal fouling), and standard BSA solution through Durapore membranes. The characteristic of pore blockage, pore constriction and cake filtration were defined and the effects of different fouling mechanism on flux decline were examined by plotting the model calculation in the form of d^2t/dV^2 vs. dt/dV that can be described by ‘blocking law’ derived by Herman et al. (1935):

$$\frac{d^2t}{dV^2} = k \left(\frac{d^2t}{dV^2} \right)^n \quad \text{Eq. 2. 10}$$

Where t is the filtration time, V is the total filtered volume and k is the proportional coefficient. n characterizes the filtration model: $n = 0$ for cake filtration, $n = 1$ for intermediate blocking, $n = 3/2$ for pore blocking, and $n = 2$ for complete pore.

Both the transition from one fouling mechanism to another and relative influence of each different fouling mechanism was predicted by these three mechanisms of fouling modeling. The model was able to assess the relative importance of each fouling mechanism, yielding more information about the filtration than a d^2t/dV^2 vs. dt/dV plot.

2. 6 Background on Techniques

2.6. 1 UV-Spectroscopy

For NOM removal monitoring the total organic carbon (TOC) measurement is the common method. However, ultraviolet light absorbance at a wavelength of 254 nm (UV_{254} absorbance) has become an accepted measurement method for the concentration of dissolved organic carbon matters (DOC). However, a correlation between UV_{254}

absorbance and DOC concentration has been observed in many studies. Organic molecules absorb UV light primarily through double bonds among carbon, oxygen, or nitrogen molecules (Carey, 1996). Although individual chromophores exhibit a distinct UV absorbance spectrum, DOM is composed of a wide mix of different compounds with different chromophores. Indeed, the most significant feature of the UV absorption spectrum of DOM is that it is a broad, featureless curve (APHA, 1998), which demonstrates that the composition of DOM is not dominated by any single compound or chromophore.

Treatment practices such as coagulation or membrane filtration may preferentially remove certain fractions of DOM; thus, removal of UV_{254} absorbance might not be well correlated with removal of bulk DOM. In this regard, the UV tests were done in triplicates, with and without syringe filtration, and the readings were consistent in all tests.

2.6. 2 Static Light Scattering Method

Comparison on Different Techniques for D_f determination

Aggregate size, density and also fractal dimension can be measured by different techniques. Three techniques of X-rays, neutrons and light scattering have all been used in the characterization of colloidal particles and in particular of fractal aggregates (Bushell, Yan et al. 2002). Of these techniques, light scattering is fast, easy and inexpensive. The wavelength of light is much longer than either X-rays or neutrons, making it more suitable for probing structures on the order of microns in size. X-Rays and neutrons are generally useful only for probing structures much smaller than a micron. The disadvantage of using light scattering is that the interpretation of the scattered intensity pattern is complicated by the strong interaction of light and matter,

and complicated theories of scattering are required for prediction. In contrast, X-rays and neutrons interact comparatively weakly with matter so that in practice a simple scattering theory such as Rayleigh Gans Debye (RGD) can always be used. Most of the past works on this method acclaimed Static Light Scattering as a reliable method (Lin, et al. 1990; Jung, et al. 1995; Park, et al. 2006).

Jung et al. (1995) compared fractal dimensions obtained from the small angle light scattering technique with those obtained from the combination of volume fraction and floc size measurement. The result showed that steady state fractal dimensions (~ 2.23) obtained by small angle light scattering was comparable to the fractal dimensions obtained from determining the slope of the relationship between floc volume fraction and floc size (2.09 and ~ 2.14). The discrepancy between the fractal dimensions obtained by these techniques during the initial stages of aggregation was understood due to the fact that the latter method measures the average fractal dimensions, whilst the former method measures the fractal dimensions at any particular instant.

Theory of Static Light Scattering

A static light scattering experiment measures the angle dependence of the scattered intensity which is denoted by $I(q)$, where the scattering wave number q is related to the scattering angle θ by:

$$q = \frac{4\pi n}{\lambda} \sin(\theta/2) \quad \text{Eq. 2. 11}$$

In this Eq., n represents the refractive index of the solvent and λ is the wavelength of light *in vacuo*. If $N(M)$ denotes the number of clusters of mass M in the scattering

volume and if interactions between the clusters are negligible, the total scattered intensity is given, up to constant factors, by:

$$I(q) = \sum N(M)I_M(q) \quad \text{Eq. 2. 12}$$

where $I_M(q)$ is the scattered intensity from clusters of mass Direct Observation Techniques.

2.6. 3 Inductively Coupled Plasma Spectroscopy (ICP-OES)

Inductively Coupled Plasma Spectroscopy - Optical Emission Spectrometer (ICP-OES) is a fast multi-element technique with a dynamic linear range and moderate-low detection limits (0.2~100 ppb). The instrument uses an ICP source to dissociate the sample into its constituent atoms or ions, exciting them to a level where they emit light of a characteristic wavelength. Up to 60 elements can be screened per single sample run of less than one minute and the samples can be analyzed in a variety of aqueous or organic matrices. Argon is used as the ICP torch gas and nitrogen is used for the optical purge gas with the Optima 2000 DV which was used for the experiments. Concentration of Na and Al ions in samples were determined by this equipment for this research work.

2.6. 4 Optical Microscope

Optical Microscope observation is not a common method for membrane fouling studies, and very few studies were done in this regard. Of all research work with microscopes, Li (1998) observed particle deposition on membrane surfaces using a

non-invasive, in situ, continuous direct observation through the membrane. An Optical Microscope (Axiolab, Zeiss) was used for direct observation. The particles used in the experiments were typical yeast and latex beads. The particle size distribution of the deposited particles changed with the cross-flow velocity, with smaller particles deposited on the membrane at higher cross-flow velocity. Comparison of the normalized flux ($J/\Delta P$) with the membrane area coverage by the particles revealed that for filtration of latex particles flux percentage (with respect to the clean membrane) was marginally greater than the percentage of uncovered membrane area, whereas for filtration of yeast, the flux percentage was significantly less than the uncovered area percentage due to the deposition of smaller cell debris species.

2.6. 5 Confocal Laser Scanning Microscope

It was reported that the only imaging technique which can avoid the problem of projecting a structure in three-dimensional space onto a plane is confocal laser scanning microscopy (CSLM), which gives a series of images representing slices taken through a sample. Since the location in space of individual particles is determined directly, it is possible in principle to measure anything about the structure including the mass fractal dimension. In practice, CSLM is limited by relatively low resolution because of its optical technology, and there are also resolution problems associated with multiple scattering. As with projection type imaging, there is also some difficulty in edge discrimination. An even more serious limitation of CSLM is that the subject must be kept quite still during the analysis, which can take 1 minute or so. This makes the technique totally unsuited to any kind of in-process examination (Bushell et al. 2002).

Recently, Park et al. (2006) developed an experimental method to determine the porosity of cake layers formed during microfiltration of aggregates made from latex

beads. The dependence of porosity on fractal geometry of aggregate was also studied. CLSM technique and subsequently image analysis was applied to measure the porosity. Aggregates were made from fluorescent polystyrene latex beads under various conditions and then their sizes and fractal dimensions were measured. Each aggregate suspension was filtered through MF membranes to form a cake layer. Experimental results showed that for the low range of fractal dimension the cake porosity may hardly depend on the fractal dimension of aggregates, but for the region of higher values it may decrease with increasing of the fractal dimension. Figure 2. 7 shows image were prepared using IMARIS. The conditions is $R=118$ $D_f=2.37$ on membrane surfaces, Pressurized at 40 kPa, scale of cross section = $506 * 506 \mu\text{m}$.

Figure 2. 7 Cakes formed from the deposition of fluorescent latex aggregates (Park, 2006).

In another study, membrane morphology were studied by CLSM (Charcosset and Bernengo 2000). Three microfiltration membranes were studied: a closed-cellular morphology (cellulose acetate membrane), a 'lacy'-like morphology (poly vinylidene fluoride), and a cylindrical pores membrane (polycarbonate). According the observations in this study CLSM was found to be a good technique since it gives a

three dimensional information of MF membranes. CSLM requires only minimal specimen preparation. Unlike SEM and TEM, it does not require any metal coating or heavy-metal staining. Three-dimensional morphology information is a unique advantage of CSLM. The optical serial sections are useful in delineating the exact morphology of the membrane. The main drawback of CLSM is providing low resolution images ($\approx 0.4 \mu\text{m}$) which does not allow to view most membrane features, especially ultrafiltration membrane structures.

Another study was done by CLSM to membrane fouling characterization during the filtration of protein solutions of protein solutions. Proteins (BSA–fluorescein and ovalbumin–Texas red conjugates) visualized in a mixture that cause fouling. Quantitative information about the presence of proteins on the surface and inside the membrane was obtained by applying image analysis algorithms and measuring parameters such as the fraction of pore surface in which protein is detected. It was asserted that the use of these results for modeling requires a statistic analysis of the number and size of the fields in the membrane to be visualized. This is particularly important when the fouling pattern of the protein is not homogeneous, but has preferential deposition–adsorption sites on the membrane. The simultaneous analysis of the results obtained through CSLM imaging combined with image analysis and macroscopic filtration data (permeate flux) enable the prevailing mechanism during fouling and the major fouling agent to be identified. Results showed internal fouling and that ovalbumin caused considerably more fouling in single and binary protein solutions than BSA (Ferrando, et al. 2005).

According to a recent study (Hwang et al. 2007) the effect of membrane fouling reducer (MFR) which is a cationic polymeric material on membrane fouling was examined in MBR systems. 3D architecture of cake as well as the spatial distribution of cellular and polymeric constituents was conducted using CLSM and image analysis technique.

CHAPTER 3 MATERIALS AND METHODS

In this chapter chemicals, materials, and methods for the study are explained.

3. 1 Chemicals

Table 3. 1 and Table 3. 2 represent specifications of the synthetic water used in the experiments and chemicals used in the experiments accordingly.

Table 3. 1 Specifications of the applied synthetic water

Name	Value
Humic Acid content	20 mg/L
Resistivity (@ 25 °C) of Ultra-pure water produced by Milli-Q purification system	18.2 M Ω .cm
pH	7
Ionic strength	10 mM as NaCl
Temperature	25 °C

Table 3. 2 Chemicals used in experiment

Name	Grade	Source	Remarks
Humic Acid (HA)	Technical	Fluka, Inc., Germany	
Alumineum Sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$)	AR	Fluka, Inc., Germany	
Ultra pure water		produced by ultra-pure water purification (UHQ, ELGA)	Resistivity of 18.2 m Ω /cm at 25° C.
Fluorescein Isothiocyanate (FITC)	AR	Fluka, Inc., Germany	Excitation wavelength: $\lambda = 490$ nm Emission wavelength: $\lambda = 525$ nm
Sodium Hydroxide (NaOH)	AR	Sigma Aldrich, Germany	
Hydrochloridric Acid (HCl)	AR	Sigma Aldrich, Germany	

3. 2 Materials

MF membrane used for this study was cellulose acetate membrane provided by ADVANTEC MFS Inc. The specifications of the membrane are shown in *Table 3. 2*. SEM image of the membrane provided by the supplier is shown in *Figure 3. 1*.

Table 3. 3 Specifications of MF membrane

Pore size	0.2 μm
Diameter	47mm
Porosity	75%
Composition	Mixture of cellulose triacetate and diacetate
Characteristics	Low static charge and high strength
Clean	Lowest aqueous extractable (0.1 wt%) of all ADVANTEC membranes

Figure 3. 1 SEM image of Millipore image of 0.2 μm MF Cellulose Acetate membranes fabricated as layers of random network of filaments. Pores are formed from the spaces between adjacent and overlapping fibers (Image provided by ADVANTEC)

3. 3 Equipments

All the equipments and analytical instruments which were used for the experiments are listed in

Table 3. 4.

Table 3. 4 Equipments applied for the experiments

Name	Model	Source	Remarks
Spectrophotometer	UV-1700 Visible, Pharma Spec	SHIMADZU Co., Japan	Data Logger: UVProbe
Static Light Scattering	Mastersizer 2000, HYDRO 2000S	MALVERN C., UK	
Inductively Coupled Plasma- Optical Emission Spectrometer	Optima 2000DV	PerkinElmer, USA	

Optical Microscope		Optical BX60	OLYMPUS OPTICAL Co., Germany	
Confocal Laser Scanning Microscope		Confocal LSM510	ZEISS Co., Germany	Software: LSM510
Analytical Instruments	pH/Conductivity/TDS/°C °F Meter	CyberScar PC300	EUTECH Ins. Singapore	
	Electronic Balance	Mettler Toledo, AG 135	SHIMADZU Co., Japan	

3. 4 Methods

3.4. 1 Preparations

A: Preparation of HA Stock Solution for Feed Water

Synthetic raw water was used in all experiments prepared by dissolving powdered humic acid in deionized water, in an amount of 20 mg/L. The preparation/pretreatment of humic acid stock solution was carried out as follows:

1 g of HA was dissolved in 80 mL of 0.1 M NaOH solution. The solution was kept overnight. Then it was diluted by 0.1 M NaOH solution to 100 mL. This solution was diluted to 900 mL with de-ionized water. Then it was kept overnight again. At the end, the solution was diluted with de-ionized water to 1000 mL.

The solution was fully mixed, and then it was firstly filtered through a paper filter and then through a 0.45 μm cellulose acetate membrane. Weight of all filters was recorded before and after filtration in a dry state in order to measure the amount of HA retained on the filter surfaces. Around 5% of the humic acid powder's weight deposited on the

filters. Therefore, 950 mg/L was the concentration of humic acid stock solution. This concentration was measured and compared with prepared standard calibration curves as well. The filtrate was transferred into a dark bottle and stored in a 4°C refrigerator for laboratory usage.

HA solution concentration that is applied in all experiments is 20 mg/L. An example of calculation for volume of 100 mL is as follows:

$$N1*V1=N2*V2 \qquad \qquad \qquad Eq. 3. 1$$

$$V2=(20 \text{ mg/L} * 100 \text{ mL})/(950 \text{ mg/L})$$

B: Preparation of Alum Stock Solution

Stock solution of alum (aluminum sulfate) was freshly prepared by dissolving analytical reagent-grade $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ in deionized water to a concentration of 2.5 g/L.

To find the proper coagulant dose, 800 mL of 20 mg/L HA solution and a predetermined volume of alum stock solution (to achieve the required dose) was added to each beaker, whereupon coagulation was carried out in 3 stages.

Calculation of the needed volume for example for 500 mL of 40 mg/L of alum is as explained by Eq. 3. 1:

$$V2=(40 \text{ mg/L} * 500 \text{ mL})/(2500 \text{ mg/L})= 8 \text{ mL}$$

C: Preparation of MF for the Test

New polymer membranes were soaked in distilled water for 1 hour prior to each run.

3.4. 2 Jar Testing

The best approach for determining the treatability of a water source and determining the optimum parameters (most effective coagulant, required dose rates, pH, flocculation times, most effective flocculent aids) is by use of a jar testing.

Jar testing protocol refer to WEF (1992) are summarized below:

Filling 800 mL synthetic raw water samples into each jar; initiating rapid mixing at 250 rpm; injecting the identified concentration of coagulant into the jars expeditiously and introduce HCl, NaOH to adjust pH 7 and consequently adding NaCl to adjust ionic strength and continue mixing at 250 rpm for an additional 1 min; after 1 min of rapid mixing, reducing the agitation intensity to 50 rpm for a duration of 20 minutes; stopping agitation, removing mixing blades from all jars and allowing flocs to settle; at the end, taking supernatant samples after 2 hours of the commencement of quiescent settling.

It should be noted that some modifications in settlement time was performed to ensure the quality of coagulation in tests.

3.4. 3 Dead-end Microfiltration Set-up

The experimental set-up consists of the jar tester for coagulation purpose, and the microfiltration set-up. The 6-paddler (2.5×6.4 cm²) Jar tester was used (STUART

Scientific Flocculator SW1, UK). The specifications of the microfiltration set-up is shown in Table 3. 4 . Figure 3. 2 shows the microfiltration set-up.

A pressurized nitrogen vessel is connected to the mini-reservoir with the capacity of 800 ml. The main feed from coagulation-flocculation is poured to this vessel. In order to keep the formed flocs in the steady condition, the feed is stirred with a magnetic stirrer in the same speed of flocculation. Dead-end stirred cell is connected to the mini-reservoir with polyethylene tubing. The liquid from the end of the vessel flows to the dead-end cell. The membrane is located in the bottom of the cell. The permeate flow to the beaker placed on an electronic balance connected to the data logging software.

Figure 3. 2 MF membrane bench-scale set-up connected to the pressurized nitrogen vessel

Table 3. 5 Specifications of bench scale MF set-up

Item	Model	Source	Material	Capacity	Maximum Operating Pressure
Pressurized nitrogen vessel					50 bars
Electronic balance	Mettler Toledo, AG 135	SHIMADZU Co., Japan			
Dead-end stirred filtration cell	Solvent Resistant Stirred Cell, Cat. No. XFUF 047 01 (47 mm)	MILLIPORE Co., USA	Borosilicate glass cylinder and 316L stainless steel base and top plate for resistance.	50 mL Holdup volume:1 mL	6 bars
Mini-Reservoir	RC800	MILLIPORE Co., USA		800 mL Holdup volume:4 mL	5.2 bars
Tubing			polyethylene		
Data logging software	TWX ReportSetting (GenTray) Filtration GraphWorkX32	ICONICS Inc., USA			

CHAPTER 4

CHARACTERIZATION OF AGGREGATES

This chapter comprises mainly characterizations conducted in this research work. Firstly it presents the UV photometric results performed to find the optimum coagulant dose for coagulation. Subsequently, sizes of aggregates as well as fractal dimension investigations are presented. Tests were performed for aggregates after coagulation and also aggregates after MF filtration. 2D and 3D images of aggregates were captured and presented in the last section of this chapter.

Results of this chapter, as preliminary data, give insights for the next step of the test that is combined coagulation-microfiltration process.

4. 1 Effect of Alum Concentration on the Removal of HA

Because the double bonds in organic molecules absorb ultraviolet light at 254nm (UV254), UV absorbance measurements can provide a quick estimate of the organic carbon content of raw or treated water samples.

UV tests were carried out after two hours of settling in coagulation and flocculation stage. Approximately 10mL of the solution was taken and filtered with 0.45 μ m membrane filter to determine the UV absorbance of the feed at λ =254 nm, at which maximum absorbance occurs, using spectroscopy method. All tests were carried out at a regulated laboratory temperature of 22–23°C at the abovementioned wavelength. Data were recorded in duplicates. Absorbance of samples for different concentrations

of alum is plotted in *Figure 4. 1*.

Absorbance trend is decreasing except for the range of 40 to 60 mg/L of alum concentration. For prepared samples in different range of alum concentration, two clear zones were observed. In clear zones the coagulation process is successful which means aggregates can be settled. First zone occurred for the sample with alum concentration of 40 mg/L, and second zone occurred for the sample with alum concentrations higher than 60 mg/L. According to Mills and Amirtharajah (1982) the first clear zone (alum concentration of 40 mg/L) indicates the charge neutralization region and the second clear zone (alum concentration higher than refers to the sweep flocculation range. In the range in-between (alum concentration between 40-60 mg/L) yellow color of solution is indicating restabilization of small aluminum hydroxide particles.

From the results, a concentration of 40 mg/L of alum was chosen for the microfiltration tests to study dead-end flux decline behavior in chapter 5. This value is the mid value of the first declining curve of absorbance. Based on the findings, this value is the minimum acceptable value of alum concentration in order to have successful coagulation.

Figure 4. 1 Coagulated sample absorbance vs. alum concentration at $\lambda = 254$

4. 2 Aggregate Size and Fractal Dimension Determination

Median size $D(0.5)$ and fractal data (D_f) were extracted out from all runs. $D(0.5)$ depicts a number being the size (in microns) at which 50% of the distribution falls below. In other words, 50% of the particles measured were less than or equal to this amount. This value was used as a representative of aggregate size in all tests. D_f , as described in the previous chapter, is defined as a parameter in relation with changes in packing density, connectivity between component particles, tortuosity, surface area, and other characteristics of an object that are observed to follow a power law with scale (Jung et al. 1995).

In the first set of experiments, static light scattering (SLS) technique is used to measure the $D(0.5)$. Mastersizer is the instrument that works with SLS technique. Statistical output data of this instrument can give a distribution of aggregate size. Stirring rate of the chamber, where sample is poured in, is fixed at the coagulation slow mixing rate. It should be mentioned that this stirring rate was also fixed (70 rpm) in the feed tank of microfiltration in order to achieve constant size of aggregates.

Samples were collected immediately after two hours of sample coagulation and gently mixed with a spatula and immediately poured to the chamber of the mastersizer for aggregate size and fractal dimension calculation. Distilled water was used as the dispersant (refractive index=1.33). Sample material properties were set as default (refractive index=1.52, absorption=0.1). Result calculation was set as a General purpose-Normal sensitivity curve. Sample and background measurement time was set 3 sec. Number of measurement cycles was 11, at 3-seconds delay between each measurement.

It should be noted that the equipment's pumping rate to suck the flow to the laser scattering section is slow due to slow paddling rate inside of the chamber is low and it is because of the slow mixing rate of the paddles in the chamber. and also due to the reaggregation process and shear force effects (Lee and Fane et al., 2003) which occurs in the chamber and piping of the equipment, it takes some minutes to get a stable value of $D(0.5)$ for each run. Due to this shortcoming of the analyzer and also complex nature of coagulation process a test tracer was carried out by adding dark blue dye to the chamber and adjusting the stirring rate of the paddle at 150 rpm (*Figure 4. 2*). It took 8 minutes (from a to c) to see the same color outlet from the piping (representing the same concentration). Another test was performed to see how the statistical size of aggregates changes by time (*Figure 4. 3*). As a result, it was found that after about 30 minutes of circulation of the sample in the instrument $D(0.5)$ achieves a very constant value of $150\mu\text{m}$. As mentioned previously, this value was calculated from size distribution of aggregates statistically.

Figure 4. 2 Malvern mastersizer equipment, inlet and outlet piping from the laser chamber($t=0$ min). a) the blue dye was seen only in inlet ($t=4$ min). b) Light blue was seen in outlet. c) dark blue was seen in outlet ($t=8$ min).

Data of the size of the aggregates ($D(0.5)$) and also fractal dimension (D_f) were collected as statistical values. The contribution of morphological characteristics of aggregates to the MF performance is studied in the next experiments by gaining these results.

Figure 4. 3 Continues trials for $D(0.5)$ measurement of 20 mg/L HA and 40 mg/L alum for 6 hours.

4.2. 1 Aggregate Size Determination

Size of aggregates can be easily changed by changing the solution chemistry. Alum was added in different concentrations to a fixed concentration of HA. In this experiment, the measurement operation is manually controlled; after cleaning (by circulating distilled water), firstly, distilled water was poured in the small stirred reservoir of the Mastersizer. Background light energy was measured in 3 cycles, and then sample is poured continually and data were recorded.

Coagulated sample was added continuously to the reservoir, and the speed of the stirrer was adjusted after seconds of circulation. After some iterations $D(0.5)$ tended to be

constant. All the measurements were run for 30 minutes. *Figure 4. 4* and *Figure 4. 5* show the records of D(0.5) before and after filtration for some iterations, and the. Measurements in this test was performed every 14 seconds and time gap between each measurement is 14 seconds. The first figure shows the D(0.5) values right after coagulation e second figure, representing after filtration, shows the D(0.5) values after coagulated feed was filtered through 0.2 μm MF under the TMP of 20 kPa. The pore size was selected based on a study of Bodzek and Konieczny (1998) that found this pore size as the optimum value in terms of flux and removal performance at the same time. After microfiltration, a brown layer of dewatered cake layer was gently collected with a sponge and then suspended in distilled water. At this stage, loose aggregates were dewatered and hence tended to be more compact. Therefore, the growth trend of aggregate size after filtration was different from that of before filtration.

Visible coagulation starts with 30 mg/L of alum. For concentrations less than this value no visible coagulation occurs. This zone referring to Amirtharajah and Mills (1982) is stable suspension zone and therefore D(0.5) is non-detectable due to insufficient coagulant dose. For the other concentrations the rising trend is observed due to coagulation process inside of the chamber.

Figure 4. 4 D(0.5) of Aggregates before filtration vs. iteration time for different concentrations of alum. D(0.5) to stay at a fixed value after 30 min.

Figure 4. 5 D(0.5) of Aggregates after filtration vs. iteration time for different concentrations of alum.

Figure 4. 6 illustrates a comparison between $D(0.5)$ of aggregates before and after filtration. The average value of $D(0.5)$ was recorded for each sample. It is obvious that the aggregate becomes smaller when it is pressurized. The diameter change is about 5 to 20 μm . For smaller aggregates, the size difference is observed to be smaller. This helps to minimize the cake layer concentration, sludge volume for disposal therefore leading to minimizing the size of the plant. This is the key target of combining coagulation to membrane filtration process in water treatment plants.

Figure 4. 6 $D(0.5)$ vs. alum concentration for aggregates before and after filtration.

From the results of *Figure 4. 6*, different mechanisms of coagulation was observed as well. For the 'Before Filtration' results, different stages of coagulation was predicted as follows: For concentrations less than 40 mg/L: charge neutralization, for concentrations between 40 & 50 mg/L: re-stabilization, and for concentrations more than 50 mg/L: sweep flocculation. Another set of experiment with a higher range of alum

concentration was operated. More exploration on the possible coagulation mechanism of coagulation will be explained with results in chapter 6.

4.2. 2 Fractal Dimension Determination

There is a long tradition of interpreting a plot of light intensity vs. scattering angle to obtain particles' morphological data. The shape of the curve has been used to provide useful information on polymer and protein conformation, via derivatives such as the Guinier plot (for globular structures), the Kratky plot (for Gaussian coils and chains) and the Bending-Rod plot for semi-flexible chains. The same principles can be applied to examine the structure of aggregates made up monomodal particles.

Providing the size of the aggregate is at least an order of magnitude greater than the primary particle size, the aggregate will obey power law scattering. In this regime a log-log plot of scattering intensity vs. wave number will give a straight line with a gradient of D_f . This plot can be obtained from the Mastersizer 2000 data if the signal response on each detector is transformed from light energy to raw scattering intensity. The angular position of the detectors within the Mastersizer 2000 system is also required (MasterSizer guideline). Mastersizer 2000 does not directly plot log-intensity vs. log-angle plots in order to establish fractal dimensions. This is achieved by exporting data into a specially prepared excel spreadsheet, which processes the standard Mastersizer 2000 export data set in order to obtain the scattering intensities measured by each detector along with the detector angles.

'Fractal Data' of aggregates at different concentrations of alum as a function of time were extracted out of the same tests for $D(0.5)$ determinations. 'Fractal Data' were put in the prepared excel worksheet, and were calculated subsequently. *Figure 4. 7* is

presented as a sample of scattering plot of aggregates. A trend line was plotted ($R=0.997$). The slope of this line represents the D_f of for each iteration.

Figure 4. 7 Scattering Plot for D_f calculation

D_f values were acquired from scattering plot of log Intensity-log Angle. These values were recorded for both cases of before and after microfiltration. *Figure 4. 8* and *Figure 4. 9* represent D_f Values of aggregates at different concentrations of alum as a function of time before and after microfiltration respectively. These values were recorded in 11 iterations with 3 seconds delay between iterations.

The fractal dimension of aggregates before filtration slightly increased as well as $D(0.5)$ trend for the aggregates before filtration. It was found that these changes are the result of flocculation process occurring in the container of mastersizer (Jung, 1995). It should be noted that for aggregates tested after filtration, which have been under TMP the trend was not the same. The D_f value was moderately fixed, and an average value of D_f was calculated in those cases. D_f value is smallest for 50 mg/L of alum concentration ($D_f = 2.1$) and for lower and higher alum concentrations its value rises reaching the maximum value $D_f = 2.61$ for alum concentration of 80 mg/L.

Figure 4. 8 Fractal Dimension (D_f) of aggregates before filtration vs. iteration time recorded for different concentrations of alum.

Figure 4. 9 Fractal dimension (D_f) of aggregates after filtration vs. iteration time recorded for different concentrations of alum.

The D_f value of aggregates (Before Filtration) was smaller (therefore less compact (Lee, Fane et al. 2003)) than D_f values of aggregates obtained from cake (after filtration) for a range of aggregates produced in different alum concentrations ranging from 30 to 80 mg/L. This result justifies the structural changes of the aggregate due to pressurization of the loose flocs. D_f values after filtration ($2.70 < D_f < 2.80$) were apparently larger than the D_f values of the flocs in solution after coagulation ($2.10 < D_f < 2.61$) than those before filtration, and this is because loose aggregates pressurized and dewatered under TMP of dead-end process.

Based on a study by Bushell, et al. (2002) as the fractal dimension increases, the role of the edge becomes more important and a transition from mass scattering to surface scattering is observed. This behavior is certain to influence the permeability of the cake and suggests that factors such as fractal dimension coupled with aggregate size will be important determinants of cake properties.

Another observation of the results was that cakes formed from the less compact floc (smaller fractal dimension) show greater tendency to compression that is in accordance to the findings of Lee and Fane (2003). As explained by these researchers, cakes made of small and loose flocs tend to have higher compressibility while cakes made of small and compact flocs are less compressible. Comparing $D(0.5)$ results (Figure 4. 7) with D_f results (Figure 4. 10), this evidence was proved.

Figure 4. 10 Fractal Dimension (D_f) vs. alum concentration for aggregates before and after filtration.

A decreasing trend of the D_f for alum concentration of less than 50 mg/L, and then an increasing trend for concentrations higher than 50 mg/L supported the statement of having different coagulation mechanisms of first, charge neutralization, then destabilization, and in the end, sweep flocculation.

4. 3 Imaging Analysis

4.3. 1 Optical Microscope Imaging

Optical Microscope was used to capture 2D images from suspended aggregates. Solution was prepared from 20 mg/L HA by adding 40 mg/L of alum as a coagulant.

Magnification adjusted on 100x. Microscope can be used in both reflection and transmission modes. In both modes polarized light can be employed for sample analysis. Immersed oil was applied in a reflection mode for sample imaging. Light brown media represents an individual aggregate in solution after coagulation process (Figure 4. 11).

A relatively broad range of aggregate sizes was captured (10-100 μ m) from the coagulated sample. Based on statistical analysis carried out by image analysis software ,which was Image-pro plus (V.6.1.0.346, Media Cybernetics Inc.), the average diameter was found to be 50 μ m which confirmed the D(0.5) results of SLS obtained by Malvern Mastersizer 2000.

Figure 4. 11 A single aggregate after coagulation taken by Optical Microscope.
Aggregate made up of HA (20mg/L)+alum (40 mg/L)

4.3. 2 Confocal Laser Scanning Microscope

The CLSM is designed for imaging with high spatial resolution. In this regard a Zeiss (LSM 510) CLSM were used. Zeiss software used for reconstruction of 3D images. Fluorescein Isothiocyanate (FITC) as a dye with excitation wavelength of $\lambda = 490$ nm was used to enhance image quality. FITC powder was added along with alum in coagulation stage. All the beakers and also dead-end filtration cell were sealed with aluminum foil in order to keep the sample out of light to preserve the florescent effects of the FITC.

By using range-indicating tool of the software, gain and offset were adjusted and the image was changed into the Black & White mode. This image can be used to quantify the porosity of aggregate. CLSM is a perfect tool to quantify porosity for microbial and biological agglomerations (Park et al., 2007). This can be reached by the unique feature of CLSM performing Z-section on specimens where it

Figure 4. 12 Aggregate suspended in solution captured by CLSM in B&W mode and it's histogram

relies on a small pinhole to block out of focus light of the microscope. Unfortunately, since cleaning of the dye was not feasible for pure organic-inorganic aggregate samples, it was impossible to capture clear and indicating images. Dye-sample separation methods such as extraction and centrifuge were tested but it was unsuccessful because aggregate breakage happened. However, this microscope successfully captured aggregates floating on the solution after coagulation.

CHAPTER 5 MICROFILTRATION BEHAVIOR

This part of work reports the flux decline behavior in dead-end microfiltration pretreated with coagulation process. Pore blocking resistance (R_p) and cake resistance (R_c) which are the dominant causes of flux decline in typical microfiltration process are quantified in sequential batches for dead-end filtration. A mathematical model was developed to describe the time dependent flux that declined and stayed constant after a short period of time.

It is claimed and mathematically proven that it is impossible to reach a steady-state flux in the dead-end filtration (Song 1998). However, by controlling the particle properties, and operational parameters, steady-state conditions were reached.

Microfiltration is a separation method based on size difference of particles, therefore all general filtration Equations can be applied in studied. According to Darcy's Law, an equation for dead-end microfiltration is derived assuming that the cake resistance is the dominant total resistance cause, the specific cake resistance is constant throughout the entire MF process, and the cut-off of the MF process that applies to the model is 100%.

$$J(t) = \frac{J_0}{\sqrt{1 + 2\phi J_0 t}} \quad \text{Eq. 5. 1}$$

Where J_0 is the initial flux, $\text{m}^3(\text{m}^{-2}\text{s}^{-1})$; ϕ is the index of membrane fouling, which can be calculated by the initial slope of $J(t)$ vs. t by Eq. 5. 2.

$$\phi = \frac{r_0 \cdot \delta_0 \cdot \Delta P^s}{R_m} = \frac{1}{J_0^2} \left. \frac{dJ}{dt} \right|_{t=0} = \frac{1}{J_0^2} \left. \frac{dJ}{dt} \right|_{t=0} \quad \text{Eq. 5. 2}$$

Subsequently an adjustable k parameter multiplied by ϕ was defined to reflect the filtration mechanism (Wang et al., 2006). It was found that variation of $k=1$ is variation of cake layer formation. They found $k=1$ for the cake filtration of kaolin, $k=4$ for yeast, $k=34.6$ for the BSA system where there is no cake layer formation on the membrane.

Al trivalent ions will bind/precipitate with HA supermolecules. The existence of loose aggregates decrease the pore blockage, which causes irreversible fouling of microfiltration. Pore blocking occurs during the initial rapid drop of flux that contributes to R_p , followed by cake formation which contributes to R_c (Song, 1998). The sequential batches of microfiltration tests were conducted to show how R_p and R_c contribute to flux decline for a long-term sequential dead-end process.

Aggregates are formed by adding 40 mg/L of alum to the feed water containing 20 mg/L HA. Flocculation/coagulation process was carried out by rapid mixing (250 rpm) for 2 minutes followed by 20 minutes of slow mixing (70 rpm). Solution chemistry was adjusted to pH=7, ionic strength 10 mM as NaCl during the rapid mixing.

5. 1 Long-term Dead-End filtration behavior

For the first step, one single run of filtration was conducted for 500 minutes. Additional feed tank (800mL) was added to the filtration apparatus in order to achieve longer filtration time. The tank includes a stirrer, which is set at 70 rpm. During the membrane

process, a high drop of permeate flux was initially observed, which gets stabilized at a constant level after some time.

Experimental data were fitted and referring simulated using MATLAB. It was assumed that the flux behaviour is polynomial to the research work of Wang (2006). Eq. 5. 2 was obtained as the best fit for experimental data with the confidence bound of 99% and R^2 of 96%. *Figure 5. 1* and *Figure 5. 2* show experimental data, their fit, and the first derivative of the fitting. The first derivative was calculated to show how fast the initial flux drops given that the first derivate value at $T=170$ min equals -0.05. This point was set as the break point for the third step of the test that includes sequential batch tests. According to Song (1998) it is assumed that before this point, the dominant process of fouling is pore blocking and after this point the dominant cause of flux drop is cake layer formation. The permeate flux decreases less rapidly as the mass of foulant on membrane increases. This is the key feature of combining coagulation process to microfiltration. Blank experiments showed that if only humic acid solution were filtered, the flux decline behavior decreased more linearly and achieved much lower value of flux. Plus, the cake layer formed with aggregates could be backwashed easily and leaded to a more reversible process.

The result of this part of the tests draws an assumption for R_c calculation. In short term dead-end tests which carried out in future experiments, R_c shall be calculated after the initial drop of the flux, when it reached a constant value.

Coagulation at pH 7, ionic strength 10mM as NaCl, TMP of 20kPa and alum concentration of 40 mg/L were selected for all runs.

$$\text{Flux} = 128.1 \times t^{-0.304} + 17.18$$

Eq. 5. 3

Where flux is in Kg/m²hr and t is in min.

Figure 5. 1 Flux decline vs. time fitted to experimental data. 20 mg/L HA+ 40 mg/L alum, at 20 kPa, membrane: 0.2 µm cellulose acetate.

Figure 5.2 (a) Fitted flux vs. time, (b) Standard 1st derivative of the model vs. filtration time

Figure 5.3 Loose aggregates accumulating on the membrane surface and forming cake layer inside of the MF cell.

5. 2 Membrane Resistance Dependence on TMP

For the second step of the experiments in this part, different resistances of the polymer membrane used in all experiments were calculated by Resistance-in-Series model.

For membrane resistance calculation 3 stages of filtration were carried out:

First, deionized water was filtered through a clean membrane. Membrane surface resistance (R_{mem}) was obtained at this stage. After 20 minutes, coagulated feed, which was continuously mixed at 70 rpm, was poured into the cell and trans-membrane pressure was applied through the nitrogen gas pump. The stirrer in the cell was on and the speed was the same as that for coagulation (70 rpm). Since feed is filtered for the first time through the membrane, the total resistance calculated out from the flux data in this stage is equal to $R_{total}=R_{mem}+R_c+R_p$. After filtration, the fouled membrane had a brown thin layer of cake. This layer was carefully wiped with sponge. The physical cleaning removed essentially the cake layer of aggregates and not the aggregates/particles blocked in pores. Therefore the yellowish color remaining on the membrane surface after physical cleaning was actually the particles entrapped in the pores of the surface of the membrane, so called the irreversible fouling. For the last stage, deionized water was poured into the cell and trans-membrane pressure was applied in order to filtrate deionized water (reversibility test). Water flux was measured again and this time the obtained resistance value represented $R_{mem}+R_p$.

It should be noted that the adsorption resistance (R_a) can also be calculated by adding the feed to the filtration cell, stirring the feed for 1 hours, then pouring the feed out and filtering DI water through the membrane. $R_{mem}+R_a$ can be calculated from the flux data, and then R_a can be calculated by subtracting the R_{mem} value gained in the first step. R_a values are measured for cellulose acetate, ceramic membrane, and aluminum coated

anodisk membranes and the values are about 2-3 orders of magnitude smaller than other resistance values. Therefore this resistance is negligible compared to R_{total} .

Flow rate of permeate was measured by timed collection using a digital balance connected to a computer. Software (TWX Report Setting GenTrey) was run for on-line data collection from the balance. Data were transferred from the balance to the computer.

Figure 5. 4 shows the R_{mem} , R_p , and R_c vs. TMP. There is a sharp change of membrane resistance values from 10kPa to 40kPa; for higher pressures resistance changes are not very significant. With the incense of the TMP, R_{mem} , R_p , and R_c increased as well. However, R_{mem} did not significantly change with varying TMP. R_{mem} is a membrane specific constant. Although it is affect by hydraulic forces due to TMP variation, but its value is not varying a lot and mechanical strength of the membrane is not affected significantly. Pore blockage, refer to R_p , and aggregate morphology is not affect by TMP. Increase of the R_c was presumably a result of compaction effects. Overll, R_c is the dominant resistance for all the tests.

Figure 5. 4 Effect of TMP on membrane resistance. Membrane is MF type cellulose acetate 0.2 μm .

Overall, as it is shown in this figure, R_c is the dominant resistance in the tests (R_p is about 10% of R_c).

Another investigation was carried out to compare deionized water (DI water) fluxes before and after filtration of synthetic water to make it possible to determine irreversible membrane fouling. Irreversible fouling of the membrane pores is created within a short time and at the initial stage of filtration cycle, and then is stabilized over a long period (Konieczny, 2002). Flux decline tests were done at 20 & 100 kPa (Figure 5. 5 and Figure 5. 6). Initial flux was 522 $\text{Kg/m}^2\text{hr}$ at 100 kPa and 136 $\text{Kg/m}^2\text{hr}$ at 20 kPa. Initial flux decline in both cases of low and high pressure was the same (about 40 $\text{Kg/m}^2\text{hr}$, normalized flux $J/J_0=1$) (Figure 5. 5) but the flux declined faster for higher TMP of 100 kPa (Figure 5.6). It can be concluded that irreversible fouling caused by coagulated feed is the same for both of the cases, and therefore, it is independent to the

TMP.

Figure 5. 5 Flux behavior of DI water filtration during the operation time.

Figure 5. 6 Reversibility test at 20 kPa & 100 kPa.

5.3 Sequential Batch Experiment

For the last step of the test, 3 sequential batches of dead-end filtration were performed with the same operating conditions using a single coupon of 0.2 μm of cellulose acetate membrane. *Figure 5. 7* shows that the starting point of all resistances is the membrane inherent resistance ($R_{\text{mem}}=5 \times 10^{11} \text{ 1/m}$). This shows that the coagulation combined with microfiltration makes the fouling reversible and the membrane can be used for many cycles of filtration.

Another point to be mentioned from the result is that the value of total resistances at 170 min for each run slightly increases and this could be because more pores are blocked after each run of cleaning. However, this change is relatively small compared to overall resistance of membrane (5%).

Figure 5. 7 Total membrane resistance of sequential batch dead-end filtration

CHAPTER 6 EVALUATION OF COAGULATION-MICROFILTRATION PROCESS

After the preliminary tests, which were described in the previous chapter, a complete set of experiments followed by characterization, concentration measurements, and microfiltration was done in the last step of this work. The through set of experiments was aimed to monitor the effect of floc size and characteristics on microfiltration performance.

In this experiment, pH & ionic strength were adjusted during the rapid mixing of coagulation. The pH was adjusted to neutral pH by adding 0.1 M NaOH and 0.1 M HNO₃ and ionic strength was adjusted to 10 mM as NaCl. Samples were collected at 6 stages as shown in *Table 6. 1* and *Figure 6. 1*.

Table 6. 1 Experimental protocol

Step No.	Sample titles	Description of experimental procedure
1	Before Settling ^a	Right after 20 minutes of flocculation, samples were collected
2	After Settling (No Filter) ^a	After 2 hours of settling, samples were collected from supernatant
3	After Settling (Filtered) ^a	After 2 hours of settling, samples were collected from supernatant and were filtered by 0.45 μ m syringe filter.
4	After Microfiltration (20 kPa) ^{a,b}	50 mL of coagulated feed filtered through 0.2 μ m cellulose acetate membrane at TMP=20 kPa. Then, the permeate was collected.
5	After Microfiltration (50 kPa) ^{a,c}	50 mL of coagulated feed filtered through 0.2 μ m cellulose acetate membrane at TMP=50 kPa. Then, the permeate was collected.
6	After Microfiltration (100 kPa) ^{a,b}	50 mL of coagulated feed filtered through 0.2 μ m cellulose acetate membrane at TMP=100 kPa. Then, the permeate was collected.

^a It should be noted that, for [Al] preservation purpose, 1 mL of HNO₃ were added into sample vials containing 13 mL of samples of ICP analyzer.

^b The stirring rate in the microfiltration cell was 150 rpm.

^c No stirring inside of the microfiltration cell was applied.

Samples were collected at both stages of before settling and after settling (supernatant) steps to see the settling effects in removal of HA on coagulation part. Again, after settling, samples were and were not filtered to see how filtration affected the readings of instruments. Because aggregates floating in the solution might disrupt the reads, especially that of UV-spectroscopy results. On the other hand, removing the aggregates from the solution might lead to incorrect readings.

Figure 6. 1 Experimental protocol explained for the complete set of experiments

6. 1 Effect of Alum Concentration on HA Removal

UV-Spectroscopy was used for measuring the humic acid concentration. For HA concentration measurement, absorbance at wavelength of 254 nm were measured first for 6 series of samples to build a calibration curve. Later, HA concentration based on the calibration curve, which was plotted previously (*Figure 6. 2*), was calculated. *Figure 6. 4* shows the results. It can be seen that the concentration level for the sample containing 20 mg/L alum is relatively higher than the rest of the samples for all 6 steps. This is because coagulation does not occur due to low concentration of alum. Concentration decreased for coagulation process of 30 and 40 mg/L after coagulation process. *Figure 6. 3* shows the $UV_{\text{removal}}\%$ that was achieved by using Eq. 6. 1:

$$UV_{\text{removal}}\% = \frac{UV_{\text{raw}} - UV_{\text{after-coagulation}}}{UV_{\text{raw}}} \times 100 \quad \text{Eq. 6. 1}$$

Where UV=UV absorbance at 254 nm.

Figure 6. 2 Calibration curve for humic acid stock solution (HA)

For concentration higher than 50 mg/L, HA could be fairly removed (more than 95%), (Figure 6. 3). Therefore, roughly, at the specific solution chemistry, for concentrations less than 50 mg/L of alum, humic acid cannot be removed from surface water only by coagulation process but for concentrations higher than this value coagulation process, removal can be done effectively only through coagulation process.

Refer to Figure 6. 3, after microfiltration, regardless of the TMP effect, removal percentage for concentrations higher than 50 mg/L is more than 95%. Removal performance is not much varying for alum concentration of 50 mg/L onward.

Figure 6. 3 UV removal rate for a range of alum concentration. pH=7, ionic strength=10mM.

Figure 6. 4 HA concentration removal for a range of alum concentration. pH=7, ionic strength=10mM.

6. 2 Mass Balance

Samples were put into the ICP analyzer after preparation. Na^+ together with Al^{+3} (alum coagulant species presumably including $\text{Al}(\text{OH})_3$, Al^{+3} and AlOH^{+2} concentration were measured by the analyzer.

Figure 6. 5 indicates the aluminum concentration of all possible aluminum species (suspended, colloidal, monomeric) for all samples. 'Before Settling' points indicate the total aluminum concentration in all forms initially, before the aggregates settled. Obviously, the values increase linearly with increasing alum concentration. For the case

of 'After settling', the concentration is relatively constant (1~2 mg/L). After microfiltration, aluminum concentration decreases to a very low level (~0.1 mg/L). Figure 6. 6 and Table 6. 2 show the removal percentage of aluminum at different stages.

Figure 6. 5 Aluminum concentration for a range of alum concentration. pH=7, ionic strength=10mM.

TMP changes do not significantly affect the microfiltration performance on Al removal. As it is better shown in *Figure 6. 6*, Al removal percentage during microfiltration process is slightly increasing from 97 to 99.5% but it is fixed for tests in different TMPs of 20, 50, and 100 kPa.

It is important to notice that even for the case of 20 mg/L of alum, which no evident coagulation occurred, Al was removed through the microfiltration process by 78.5%. In this case presumably there is no aluminum precipitate or bonded Al^{+3} to HA.

Al concentration before and after settling is very close as shown in Table 6.2 (2.08 and 2.05 mg/L respectively). Al concentration value is minimum for the filtered case.

Table 6. 2 Al concentration in different stage1.1s of process

Sample Tag	Al Concentration (mg/L)
Before Settling	2.08
After Settling (No Filter)	2.05
After Settling (Filtered)	0.15
After Microfiltration (20 kPa)	0.95
After Microfiltration (50 kPa)	0.51
After Microfiltration (100 kPa)	0.45

Figure 6. 6 Aluminum removal percentage for a range of alum concentration. pH=7 & ionic strength=10mM

In order to measure the accumulated mass on the membrane (mass calculation), sodium (Na) concentration was measured in all the stages of the experiment. *Figure 6. 7* displays the results. The Na removal was seen due to Na^+ bonding to the aggregates, although it was not significant.

Figure 6. 7 Sodium concentration for a range of alum concentration. pH=7, ionic strength=10mM

6. 3 Characterization of Aggregates

Figure 6. 8 shows the records of D(0.5) after one hour. D(0.5) of aggregates for a range of alum concentration was recorded for all samples on different alum concentration. The stirring rate was adjusted at 150 rpm.

It is shown that aggregate size dramatically changes by changing the Al concentration. The D(0.5) value range widely starting from 100-500 μm . But it should be noted that these data were acquired at stirring rate of 150rpm speed of paddle rate of the equipment. Therefore the aggregate size is larger than the values recorded. These data actually are the dynamic diameter of aggregates.

Visible coagulation starts at 30 mg/L of alum. For concentrations less than this value no

visible coagulation occurs. This zone is called stable suspension zone and therefore $D(0.5)$ is not detectable due to insufficient coagulant dose (Amirtharajah, Mills 1982). For the other concentrations a strictly rising trend was observed due to coagulation process inside of the chamber.

Fractal dimension was not studied in this set of experiments because according to the preliminary studies (Chapter 4), fractal dimension did not vary for the aggregate prepared in the composition and concentration range of our tests. If smaller aggregates were present, fractal dimension effect on aggregate size would be more evident (Guan et al., 2001).

Figure 6. 8 Size of aggregate for a range of samples (20-100 mg/L) formed of different alum concentration.

6. 4 Microfiltration Results

6.4. 1 Permeate Flux Decline Trends

Flux behavior of low and high TMPs for microfiltration process at 20 & 100 kPa is shown in *Figure 6. 9* and *Figure 6. 10* respectively.

At low TMP (20kPa) and for alum concentration of 20 mg/L, flux values are relatively close for all concentrations of alum, but at high TMP (100 kPa) the flux declined faster (about half of its value) compared with the other samples, although initial flux is the same for all concentrations. Based on the results in this part, it can be concluded that at higher TMP coagulation process as a pretreatment is much helpful in fouling mitigation rather than low TMPs (20 kPa).

Because all the feed solutions were filtered with the same volume of 50 mL, flux time is much lower (again, about half of its value compared to 20 mg/L of alum in the feed).

Figure 6. 9 Permeate flux of microfiltration vs. time. 50 mL of coagulated feed in a range of alum concentrations was filtered (TMP=20 kPa).

Figure 6. 10 Permeate flux of microfiltration vs. time. 50 mL of coagulated feed in a range of alum concentrations was filtered (TMP=100 kPa).

6.4. 2 Total Resistance & Specific Cake Resistance results

In order to calculate the R_{cake} from the flux data, total resistances (R_{total}) of membrane were calculated firstly from *Eq. 2. 1* and *Eq. 2. 2*, and then specific cake resistance calculated. First, R_{mem} was subtracted from R_{total} and from the results obtained and demonstrated in *Figure 5. 4*, R_p value was assumed to be negligible and equal for all values of R_{total} for the whole range of alum concentration. Therefore it was neglected in the calculations. Specific Cake Resistance (α_c) was then calculated using *Eq. 2 .3*, where R_{cake} is assumed to be $R_{\text{total}} - R_{\text{mem}}$. A is the filtration effective area with the disc membrane diameter of 43 mm, and m_p is the accumulated mass on the membrane which was calculated by mass balance calculation as it is shown:

$$m_p = \sum_{i=1}^3 C_{in} V_{in} - \sum_{i=1}^3 C_{out} V_{out} \quad \text{Eq. 6. 2}$$

Concentration of all elements (C_{in} & C_{out}) were acquired by ICP-OES and concentration of HA molecules were acquired by UV-VIS ($i=1,2,3$ for Al, Na, HA which are main components present in the solution and remaining on the cake). The inlet volume (V_{in}) was 50 mL, and the outlet Volume (V_{out}) with some errors was assumed to be 50 mL as well.

The results are shown in *Figure 6. 11* which are obtained at TMP=20 & 100 kPa. At both low and high TMPs the same trend can be observed by dividing it into two parts of lower than 40 mg/L of and higher than 40 mg/L of alum concentration:

Figure 6. 11 Variation of Specific Cake Resistance as a function of alum.

For alum concentrations lower than 40 mg/L, results were in accord with the modified Carman-Kozeny relationship (Guan et al., 2001). In addition, mastersizer results approves the relationship between size of aggregates, and membrane resistance for low range of alum concentration, $D(0.5)$ and α_c declined accordingly.

Coagulation mechanism in this section is via charge neutralization (Kim et al., 2007). Al^{+3} concentration was less than saturation level; therefore no precipitate was formed. Chemical reaction between positively charged Al^{+3} was ions and negatively charged HA particles formed aggregates. Size of the aggregates based on $D(0.5)$ results of mastersizer shows a declining trend and it is supposedly because less share of Al^{+3} attached or bonded to HA and it makes aggregates smaller in diameter. Second part, at alum concentrations higher than 40 mg/L, the $D(0.5)$ value increased with increasing alum concentration. For alum concentrations higher than 40 mg/L coagulation mechanism changed to sweep flocculation. $Al(OH)_3$ precipitates agglomerated the HA molecules and formed the aggregates.

α_c values did not change and remained slightly fixed by increasing the aggregate size. Although aggregate size increases with increasing alum content, this does not affect the filtration performance in terms of membrane specific cake resistance. Therefore, from the results, when the dominant mechanism of coagulation is sweep flocculation, size of aggregates did not affect the membrane cake resistance (R_c) and membrane specific cake resistance (α_c) (Lee and Fane, 2003). This assumption was explained by calculating the HA/Al ratio on the cake deposited on the membrane in *Figure 6. 12*. Power regression fitted quiet well with this trend ($y = 10.114x^{-0.7315}$ $R^2 = 0.9801$). $[HA]/[Al]=9$ was observed for the case of 20 mg/L of alum addition which no visible coagulation occur that very few ions of aluminum was attached to the HA molecules. For alum concentrations of 30 & 40 mg/L (charge neutralization region) this ratio decreased to 7 and 5, but these values are still high compared with the rest of the

samples with higher concentration of alum dosing which resembles sweep flocculation region and the ratio was the range of 2~4.

Figure 6. 12 [HA]/[Al] deposited on the cake layer for a range of concentration on alum

CHAPTER 7

CONCLUSION AND RECOMMENDATIONS

7.1 Conclusions

Different coagulation mechanisms which leads to form different aggregate structures that consequently lead to different aggregate fouling performances were investigated.

Alum dosing concentration of 40 mg/L for the synthetic feed water solution obtained as the optimum coagulant dose. High removal efficiency of HA (95%) and also Al^{+3} removal of 97.5% (equals to concentration less than 1 mg/L which meets the drinking water standards) was achieved.

Fractal dimension (D_f) did not changed significantly with various aggregate size variation. However, fractal dimension was larger for loose aggregates compared to the compressed ones at certain TMP. This means that aggregates were dewatered, and this shows the other important benefit of the combined Coagulation-Microfiltration process in terms of sludge minimization for disposal.

Fouling was investigated by measuring the flux and consequently membrane resistances over a period of filtration time that initial sharp flux decline ended and the process becomes close to steady-state conditions. Flux plotted against filtration time for a range of alum dose and TMP found to be the most affecting parameters for filtration performance.

Coagulation pretreatment for microfiltration process was found to be useful for mitigation of membrane fouling problem. Results showed that membrane pore blocking

resistance (R_p) that causes membrane irreversible fouling could be decreased to a satisfying low level compared to membrane cake resistance which easily can be cleaned by back washing.

Pseudo steady-state condition was achieved for dead-end filtration of humic acid and alum. We have shown that pore blocking plays an insignificant role in flux decline in coagulation-microfiltration system when alum is present compared to the case that only humic acid is present (results not shown here). These results give insights to more economically feasible process for surface water treatment.

Nature of aggregates studied and correlated to the results of microfiltration flux trend for short term which resembles initial flux decline behavior that increased with pore blocking and also long term behavior that leads to higher membrane specific cake resistance.

Based on the results of the full set of coagulation-microfiltration, it is concluded that at higher TMP coagulation process as pretreatment is more helpful in fouling mitigation rather than at lower TMPs (20 kPa) because at high TMP (100 kPa).

In order to enhance the performance of the coagulation-microfiltration process, the nature of foulant matters (aggregates in this system) is highly affected by operational and physicochemical parameters. It realized that there is a high potential of studying the characterization of aggregates after coagulation process and also packed layer of aggregates on the membrane surface after microfiltration.

Static Light Scattering was found to be a useful method to measure the dynamic diameter, weight density, and fractal data of even very loose aggregates.

The results of D(0.5) trend and also UV-spectroscopy trend for increasing dosage of coagulant both justified the phenomenon of different mechanism of agglomeration of HA macromolecules with aluminum constituents and precipitates, by changing the water chemistry variables as pH and ionic strength.

Subsequent result of dead-end microfiltration showed that based on the type of coagulation (charge neutralization, sweep flocculation) the concentration of coagulant added should be optimized to reach optimal flux rate and minimum cake resistance.

7. 2 Further Perspectives and Recommendations

The porosity of aggregates could be quantified by CLSM, using appropriate dye and appropriate methods in order to separate the fluorescent solution from aggregates.

By using the Fluorescent Intensity Measurement tool provided with CLSM, fluorescent intensity can be measured. Density vs. intensity could give information on the porosity of the sample. No research work has focused on it for pure organic-inorganic aggregates (not biological) up to today. After capturing images in different chemical and operational conditions, and conducting a comparison on the morphology of aggregates can give useful information on characterization of aggregates

REFERENCES

APHA, AWWA, and WEF (1998) (American Public Health Association, American Water Works Association, and Water Environment Federation). Standard Methods for the Examination of Water and Wastewater. 18th ed. Washington, D.C.:APHA.

Application Report, Mastersizer 2000 Fractal dimension calculation.

AWWA. (2005) "Microfiltration and Ultrafiltration Membranes for Drinking Water", 1st Edition. American Water Works Association, Denver, Colorado.

Amal, R., J. A. Raper, et al. (1990). "Fractal Structure of Hematite Aggregates." Journal of Colloid and Interface Science 140(1): 158-168.

Amirtharajah, A., Mills, Kirk M. (1982) "Rapid-Mix Design for Mechanisms of Alum Coagulation" Water Work Association 74(4):210-216.

Belfort, G., Davis, R. H. and Zydney, A. L. (1994). Behaviour of Suspensions and "Macromolecular Solutions in Crossflow Microfiltration". Journal of Membrane Science, 96, 1-58.

Bodzek, M. and K. Konieczny (1998). "Comparison of various membrane types and module configurations in the treatment of natural water by means of low-pressure membrane methods." Separation and Purification Technology 14(1-3): 69-78.

Bushell, G. C., Y. D. Yan, et al. (2002). "On techniques for the measurement of the mass fractal dimension of aggregates." Advances in Colloid and Interface Science 95(1): 1-50.

Carey, F.A. 1996. Organic Chemistry. McGraw-Hill: New York, NY.

Carman (1938). "Fundamental principles of industrial filtration", Transactions of the Institution of Chemical Engineers 16:168–188.

Carrol, T., S. King, S. R. Gray, B. A. Boltom and N. A. Booker (2000). "The Fouling of microfiltration membranes by NOM after coagulation treatment" Water Resources 34(11): 2861-2868.

Charcosset, C. and J. C. Bernengo (2000). "Comparison of microporous membrane morphologies using confocal scanning laser microscopy." Journal of Membrane Science 168(1-2): 53-62.

Chen, D., L. K. Weavers, et al. (2006). "Ultrasonic control of ceramic membrane fouling caused by natural organic matter and silica particles." Journal of Membrane Science 276(1-2): 135-144.

Chen, J. C. and A. S. Kim (2006). "Monte Carlo simulation of colloidal membrane filtration: Principal issues for modeling." Advances in Colloid and Interface Science 119(1): 35-53.

Choi, K. Y. J. and B. A. Dempsey (2004). "In-line coagulation with low-pressure membrane filtration." Water Research 38(19): 4271-4281.

Croue, J.P., Debroux, J.F., Amy, G.L., Aiken, G.R., and Leenheer, J.A. (1999). Natural Organic Matter: Structural Characteristics and Reactive Properties. Formation and Control of Disinfection By-Products in Drinking Water. P.C. Singer. Denver, AWWA:65-94.

Dentel, S. K. and J. M. Gossett (1988). "Mechanisms of coagulation with aluminum salts." Journal American Water Works Association 80(4): 187-198.

Duan, J., N. J. D. Graham, et al. (2003). "Coagulation of humic acid by ferric chloride in saline (marine) water conditions." Water Science and Technology 47(1): 41-48.

Duan, J. M., J. H. Wang, et al. (2002). "Coagulation of humic acid by aluminium sulphate in saline water conditions." Desalination 150(1): 1-14.

Duclos-Orsello, C., W. Y. Li, et al. (2006). "A three mechanism model to describe fouling of microfiltration membranes." Journal of Membrane Science 280(1-2): 856-866.

Farahbakhsh, K., Svrcek, C., Guest, R.K. and Smith, D.W. (2004). A Review of the Impact of Chemical Pre-treatment on Low-Pressure Water Treatment Membranes. Journal of Environmental Engineering and Science 3:237-253.

Guan, J., R. Amal, et al. (2001). "Effect of aggregate size and structure on specific resistance of biosolids filter cakes." Water Science and Technology 44(10): 215-220.

Hwang, B. K., W. N. Lee, et al. (2007). "Effect of membrane fouling reducer on cake structure and membrane permeability in membrane bioreactor." Journal of Membrane Science 288(1-2): 149-156.

Jiang, J. (2001). "Development of Coagulation Theory and Pre-Polymerized Coagulants for Water Treatment." Separation and purification method 30(1): 127-141.

Jones, K. L. and C. R. O'Melia (2000). "Protein and humic acid adsorption onto hydrophilic membrane surfaces: effects of pH and ionic strength." Journal of Membrane Science 165(1): 31-46.

Jung, S. J., R. Amal, et al. (1995). "The use of small angle light scattering to study structure of flocs." Particle & Particle Systems Characterization 12(6): 274-278.

Kim, H. C., J. H. Hong, et al. (2006). "Fouling of microfiltration membranes by natural organic matter after coagulation treatment: A comparison of different initial mixing conditions." Journal of Membrane Science 283(1-2): 266-272.

Kim, I. H., N. Yamashita, et al. (2009). " Discussion on the application of UV/H₂O₂, O₃ and O₃/UV processes as technologies for sewage reuse considering the removal of pharmaceuticals and personal care products." Water Science & Technology 59(5): 945-955.

Kokkola, H., Sorjamaa, R., Peraniemi, A., Raatikainen, T. and Laaksonen, A. (2006) Cloud Formation of Particles Containing Humic-like Substances. Geophysical Research Letters 33(10): L10816

Konieczny, K., M. Bodzek, et al. (2006). "A coagulation - MF system for water treatment using ceramic membranes." Desalination 198(1-3): 92-101.

Konieczny K. (2002). "Modelling of membrane filtration of natural water for potable purposes" Desalination 143(2002): 123-139.

Kyllonen, H. M., P. Pirkonen, et al. (2005). "Membrane filtration enhanced by ultrasound: a review." Desalination 181(1-3): 319-335.

Laîné, J.M, Vial, D. and Moulart, P. (2000). "Status after 10 years of Operation – Overview of UF Technology Today. Proceedings of the Conference on Membranes in Drinking and Industrial Water Production, Volume 1, Desalination Publications, L'Aquila, Italy. Paris, France: 17-25.

Lee, S. and J. Cho (2004). "Comparison of ceramic and polymeric membranes for natural organic matter (NOM) removal." Desalination 160(3): 223-232.

Lee, J. D., S. H. Lee, et al. (2000). "Effect of coagulation conditions on membrane filtration characteristics in coagulation-microfiltration process for water treatment." Environmental Science & Technology 34(17): 3780-3788.

Lee, S. A., A. G. Fane, et al. (2003). "The effect of floc size and structure on specific cake resistance and compressibility in dead-end microfiltration." Separation Science and Technology 38(4): 869-887.

Lee, S. Y. A., A. G. Fane, et al. (2005). "Impact of natural organic matter on floc size and structure effects in membrane filtration." Environmental Science & Technology 39(17): 6477-6486.

Lerch, A., S. Panglisch, P. Buchta b et al. (2005), "Direct river water treatment using coagulation/ceramic membrane microfiltration." Desalination 179: 41-50.

Li, H., A. G. Fane, et al. (1998). "Direct observation of particle deposition on the membrane surface during crossflow microfiltration." Journal of Membrane Science 149(1): 83-97.

Lin, M. Y., R. Klein, et al. (1990). "THE STRUCTURE OF FRACTAL COLLOIDAL AGGREGATES OF FINITE EXTENT." Journal of Colloid and Interface Science 137(1): 263-280.

McDonogh, R. M., C. J. D. Fell, et al. (1984). "SURFACE-CHARGE AND PERMEABILITY IN THE ULTRAFILTRATION OF NON-FLOCCULATING COLLOIDS." Journal of Membrane Science 21(3): 285-294.

Meakin, P., (1988). "Fractal aggregates. *Advances in Colloid and Interface Science*" 28:249–331.

Molinari, R. , L. Palmisano, et al. (2002). "Studies on various reactor configurations for coupling photocatalysis and membrane processes in water purification." Journal of Membrane Science 206(1-2): 399-415.

MWH. (2005). *Water treatment – Principles & Design*. 2nd Edition. John Wiley and Sons, Inc, NY.

Oh, H. K., S. Takizawa, et al. (2007). "Removal of organics and viruses using hybrid ceramic MF system without draining PAC." Desalination 202(1-3): 191-198.

Park, P. K., Ch. H. Lee, S. Lee et al. (2007) "Determination of cake porosity using image analysis in a coagulation–microfiltration system" Journal of Membrane Science 293(1-2): 66–72

Park, C., H. Kim, et al. (2006). "Variation and prediction of membrane fouling index under various feed water characteristics." Journal of Membrane Science 284(1-2): 248-254.

Park, N., B. Kwon, et al. (2006). "Characterizations of the colloidal and microbial organic matters with respect to membrane foulants." Journal of Membrane Science 275(1-2): 29-36.

Park, P. K., C. H. Lee, et al. (2006). "Permeability of collapsed cakes formed by deposition of fractal aggregates upon membrane filtration." 40(8): 2699-2705.

Park, P. K., C. H. Lee, et al. (2006). "Variation of specific cake resistance according to size and fractal dimension of chemical flocs in a coagulation-microfiltration process." Desalination 199(1-3): 213-215.

Peuchot, M. M. and R. Benaim (1992). "Improvement of Cross-Flow Microfiltration Performances With Flocculation." Journal of Membrane Science 68(3): 241-248.

Piccolo A., (2002) "The Supramolecular structure of humic substances. A novel understanding of humus chemistry and implications in soil Science". Advances in Agronomy, 75:57-134.

Richens, D.T. (1997). The Chemistry of Aqua Ions, Wiley: Chichester.

Schippers J.C., J. Verdouw (1980). "The Modified Fouling Index, A Method of Determining Characteristics of water." Desalination 32: 131-148.

Thurman, E.M. (1985). Organic Geochemistry of Natural Waters. Dordrecht, Netherlands, Martinus Nijhoff/Dr. W. Junk Publishers.

Veerapeni, S.; Wiesner, M. R. (1996) "Hydrodynamics of fractal aggregates with radially varying permeability." Journal of Colloid and Interface Science 177: 45-57.

Vial, D., Doussau, G. (2002). "The use of microfiltration membranes for seawater pre-treatment prior to reverse osmosis membranes." Desalination 153: 141-147.

Wang, Zh., , Liu D., Wu W., Liu M. (2006). "Study of dead-end microfiltration flux variety law." Desalination 201: 175–184.

WEF (1992) Standard Methods for the Examination of Water and Wastewater, 18th Edition.

Zhang, G. H., Y. Gao, et al. (2005). "Removal of fluoride from drinking water by a membrane coagulation reactor (MCR)." Desalination 177(1-3): 143-155.